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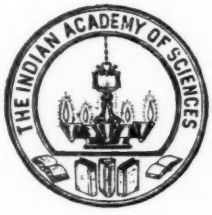

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REFLECTION OF X-RAYS WITH CHANGE OF FREQUENCY

Part I. Theoretical Discussion

By Sir C. V. Raman and Dr. P. Nilakantan

(*From the Department of Physics, Indian Institute of Science, Bangalore*)

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1. Introduction

The present paper deals with the new type of X-ray reflection in crystals observed by the authors and described in an address to the Easter Conference of Scientific Societies at Bangalore on the 22nd March of this year. A brief account of the phenomenon with an illustrative photograph of the effect as observed in diamond appeared as a special article[1] in the issue of *Current Science* for April under the title "A New X-Ray Effect". The phenomenon was there described as having "in its physical nature, something in common with both the Laue and the Compton effects", and as being "a specular reflection of X-rays by crystals but with a change of frequency explicable only on quantum mechanical principles". More succinctly, we may describe it as the analogue in X-ray optics of the phenomenon of the scattering of light in crystals accompanied by a change of frequency. The appropriateness of these descriptions will be made evident as we proceed.

Twenty-two photographs grouped in eight plates accompany Parts II and III of the present paper (appearing in the same issue) and are intended to illustrate various aspects of the new phenomenon. Detailed studies have been made with two crystals, namely, diamond and sodium nitrate, which fully establish the nature of the effect and confirm the theoretical interpretations which have been put forward. These are also set out with full particulars.

2. Scattering of Light in Crystals

In the lecture[2] on "A New Radiation" (Raman, 1928) describing the phenomenon of a change of frequency in the scattering of light by matter, the issue was raised whether such scattering should be considered as being coherent or non-coherent radiation, in other words, whether the different molecules in the substance emit the scattered radiation with or without any definite phase-relationships as between themselves. It was suggested that

though the assumption of incoherence might seem a natural one to make, nevertheless the question required investigation before a definite answer could be returned. Considering the purely theoretical issue, it is evident that if the molecules in a substance are independent oscillators, the scattered radiations arising from the transfer of energy to them need obviously have no specifiable phase-relationships. The position would however be different when the molecules are packed and held together as an ordered assemblage in a crystalline solid by interatomic forces. In such a case, the oscillations with which we are concerned would be those of the crystal lattice rather than those of the individual atoms or molecules. The transfer of energy from the radiation to the substance should then evidently be regarded as a process in which the crystal as a whole is the operative unit. This point of view was indeed suggested and adopted[3] by Ig. Tamm (1930) as the basis for a quantum-theoretical discussion of light-scattering in crystals.

The simplest mechanism by which a change of frequency can be produced in light by the co-operative action of the molecules in a substance is that considered many years ago by Leon Brillouin[4] in a well-known paper (1922). Addressing himself to the problem of the diffusion of light by the thermodynamic fluctuations of density in a substance, Brillouin considered the effect on a beam of light of a plane train of sound-waves traversing the medium. The sound-waves result in a periodic stratification of the optical density of the medium, and hence in accordance with a well-known optical principle would selectively reflect the light-waves, provided these are incident on the stratifications at a glancing angle θ satisfying the relation

$$2\lambda^* \sin\theta = \lambda \tag{1}$$

λ and λ^* are the wave-lengths of light and sound respectively as measured in the medium. The optical stratifications due to the sound-waves are, however, not static but travel through the medium with the usual acoustic velocity v. Accordingly, there would be a Doppler effect giving a change of frequency in the reflected light. This would be an increase or a decrease according as the sound-waves approach or recede from the light source. The change of frequency is given by the usual formula for reflection from a moving mirror, namely,

$$\nu_{\text{reflected}} - \nu_{\text{incident}} = \pm 2 \cdot \nu \cdot \frac{v}{c} \sin\theta \tag{2}$$

c being the velocity of light in the medium. Writing $c = \nu\lambda$ and $v = \nu^*\lambda^*$ where ν and ν^* are the frequencies of the incident light and sound-waves respectively, and combining equations (1) and (2), we have the relation,

$$\nu_{\text{reflected}} - \nu_{\text{incident}} = \pm \nu^* \tag{3}$$

In other words, the change in the frequency of light in a Brillouin reflection is merely the frequency of the periodic pulsation in the optical density of the medium.

In the case considered by Brillouin, the sound-waves are those spontaneously existing as the result of the thermal agitation in the substance. The wave-length λ^* of the sound which is actually operative is automatically determined by the wave-length λ of the light and the glancing angle θ as per equation (1). As λ^* diminishes from ∞ to $\lambda/2$, θ varies from 0 to $\pi/2$, and hence the specular reflection by the sound-waves actually gives a scattering in all directions with a change of frequency depending on the direction as indicated by (2). As the velocity of sound is small compared with that of light, this change of frequency is also small. Nevertheless, it has been established experimentally for the case of light-scattering in liquids, and more recently[5] also in crystals (Raman and Venkateswaran, 1938).

It should be remarked, that the optical principles on which equations (1) and (2) rest are of very general validity, and we are not therefore restricted to the cases in which the dynamic stratification in the medium may be identified with ordinary sound-waves. We may, in fact, start from (3), and consider a case in which a pulsation of optical density occurs in the medium with a specified frequency ν^* which may be much higher than that of any sound-waves permissible in the medium. We may assume further that the pulsation, instead of occurring with identical phase throughout the otherwise homogeneous medium, appears as a periodic stratification having a wave-length λ^* and travelling through the medium with a phase-velocity which is not identical with the ordinary acoustic velocity and indeed may be vastly greater. The stratifications would then give rise to a reflection of the incident light-waves with a change of frequency ν^* as in the case already considered, provided that the wave-length of the stratifications and their inclinations to the incident light-waves satisfy the relation (1).

The foregoing discussion indicates that when light is scattered by a homogeneous crystalline solid with a change of frequency ν^* corresponding to one or other of the characteristic infra-red frequencies, the process which occurs may be pictured as follows : The effect of incidence of the light-waves on the crystal is to generate in the latter, periodic stratifications of optical density having the frequency ν^* and a wave-length λ^*, the latter depending on their inclination to the light-waves. These stratifications reflect the light with altered frequency in the manner indicated by equations (1) and (3). The appropriate wave-length of the stratifications and their inclination to the incident light-waves are determined by the act of reflection itself.

Surprising as this picture may seem, it is difficult to avoid the acceptance of it, once we concede the idea that the process of light-scattering in a crystal is a coherent phenomenon. Indeed, it is obvious that a completely homogeneous medium can scatter no light even if it is pulsating periodically. The presence of appropriately spaced and inclined stratifications of the pulsation is therefore a necessity to explain the observed scattering.

We may, at this stage, well ask ourselves the question, is there any experimental evidence to support the basic postulate of coherence? It should be remarked in this connection, that measurements of the intensities of the scattered radiations cannot furnish a direct reply to this question. At first sight, it might seem that 'coherent' scattering should give us a much larger scattering than the 'incoherent' variety, and indeed this would be the case if the strength of the optical dipoles in the scattering particle is prescribed beforehand. Actually, however, when numerous oscillators co-operate in taking up energy from the incident quantum of radiation, their individual dipole strengths are reduced in proportion, and hence, when they emit the quantum again in co-operation, the final result is practically unaffected. The evidence actually available which indicates that light-scattering in crystals is a coherent process is rather indirect. It is well known that the frequency shifts given by crystals often differ appreciably from those obtained in the gaseous or liquid condition of the same substance, and are generally represented by sharply defined lines in the spectrum. Further, the selection rules for the intensity and polarisation of the scattered radiations appear, at least in the cases so far examined, to be determined by the structure and symmetry of the crystal as a whole, rather than by the structure and symmetry of the ionic or molecular units contained in it. These facts are significant and clearly favour the coherence hypothesis. This evidence is however, not absolutely conclusive and we have to rely more on the *a priori* probabilities of the case. If we consider a crystal such as diamond or quartz consisting of chains of atoms linked together firmly and continuously by valence bonds, it would be difficult to concede that the scattering of light in it could be the result of incoherent local processes involving only individual atoms. Such a crystal as diamond or quartz has been aptly described as being itself a giant molecule, and it appears quite natural to regard the solid as a whole and not the individual atoms in it as the scattering units. Indeed it may be said that nothing so far observed definitely contradicts the postulate of coherence in light-scattering as applied to crystals.

3. *Effect of Pulsation of Structure-Amplitude*

In his paper of 1922, Brillouin applied his theory of reflection by sound-waves to the problem of the diffusion of X-rays when passing through a

crystal which results from the thermal agitation in it. It is clear from equation (1) that such reflections would, as in the case of light, give rise to a diffusion or scattering of the radiation. But owing to the short wave-length of the X-rays, such diffusion would be limited to glancing angles ranging from zero up to a maximum determined by the shortest wave-length of sound present in the acoustic spectrum of the crystal. As this wave-length limit for sound can scarcely be smaller than the grating constant of the crystal, the diffusion of the Brillouin type would be limited to glancing angles less than that at which any Bragg reflection of monochromatic X-rays by the crystal could appear.

As in the case of light, however, we are not restricted to considering stratifications which are identifiable with sound-waves, and may extend the application of equations (1), (2) and (3) in the X-ray region to any type of coherent pulsation capable of giving periodic stratifications of the electron density of the crystal. Excluding the case of small glancing angles, we see from (1) that the wave-length λ^* of the stratifications must be comparable with that of the incident X-rays, and would therefore also be of the same order of magnitude as the crystal spacings existing in solids which give the ordinary Bragg reflections of unchanged frequency. It is therefore necessary to consider in what circumstances, the dynamic X-ray reflections with change of frequency here contemplated may be expected to occur with sensible intensity and be capable of being distinguished from the usual static reflections.

As is well known, the usual Laue spots given by X-rays with crystals are observed when the Bragg condition given by (1) is satisfied, λ^* now representing the spacings in the crystal structure, and λ the wave-length of the X-rays responsible for the reflection. The intensity of any such reflection is determined principally by a quantity known as the structure-amplitude of the spacing, which appears as a multiplying factor of the corresponding term in the three-dimensional Fourier analysis of the electron density in the crystal. This structure amplitude is determined by the atomic arrangement in the unit cell of the crystal lattice. If, now, we postulate a periodic pulsation of the atomic positions in all the cells of the crystal lattice, its effect would be to vary the structure-amplitude of every spacing of the crystal periodically with the same frequency. In other words, the effect of such pulsation is to superimpose upon the each static structure-amplitude of the crystal, a dynamic structure-amplitude having the same spacing and capable of giving a reflection with changed frequency.

We may now, in the first instance, consider the consequences of assuming that the phase of the pulsation of electronic density is rigorously the same

for all the unit cells in the crystal lattice. The static and dynamic stratifications of electron density would then everywhere run parallel to each other, and the geometric conditions (as given by the Bragg formula) for the appearance of static and dynamic X-ray reflections would therefore be identical. In other words, the unmodified and modified X-ray reflections would always appear or fail to appear, at the same time. Since the actual change of frequency in the X-ray reflections is beyond the resolving power of the most powerful X-ray spectrometer, we should be unable to detect the appearance of the modified reflections in the presence of the unmodified ones.

Actually, however, the assumption that the pulsations in the cells of the crystal lattice are coherent does not imply that their phases should be identical at all points of the crystal. Indeed, we have already seen that in order to explain the phenomena observed with ordinary light, it is necessary that the analogous pulsations of optical density in the crystal should *not* be of identical phase throughout, but should appear as stratifications having the appropriate wave-length and inclination to the incident light-waves and thus satisfying the condition for a coherent reflection. In our present case, the spacing or wave-length of the dynamic stratifications is fixed, being in fact the atomic spacings in the crystal, but their phases are capable of adjustment and should, in fact, automatically adjust themselves, as in the case of light, so as to secure the condition necessary for reflection. *It is readily seen, that a progressive change of phase in the atomic pulsations as we move in a direction parallel to a particular plane of atoms is equivalent to a tilt of the wave-front of that pulsation away from the crystal planes in a direction perpendicular to them.* When a pencil of X-rays is incident obliquely on a particular spacing of the crystal, the phase of the electrical vibration reaching successive atoms in any particular layer alters progressively in the plane of incidence. A compensating change in the phase of the structure-amplitude variation along the same direction would, in effect, tilt the wave-fronts of the atomic pulsation to such an obliquity that the Bragg condition for the particular spacing may be satisfied. In other words, we can get a dynamic or modified X-ray reflection from a particular atomic spacing at an angle of incidence at which we cannot obtain the usual Bragg reflection for the same X-ray wave-length. The modified reflection would in these circumstances appear in a direction which is displaced from the usual geometric position.

The foregoing discussion indicates that the unmodified and modified X-ray reflections are separable by the simple device of tilting the crystal away from the correct glancing angle for the X-ray wave-length employed. The unmodified reflection obeys the usual geometrical laws of reflection from

the atomic spacings besides satisfying the Bragg condition. The modified reflection also appears in the plane of incidence of the X-ray on the atomic spacings, but in general, in a direction different from that of geometric reflection from such planes. This failure of geometrical optics is, however, more apparent than real; as we have already seen, the modified reflections satisfy both the geometrical laws of reflection and the Bragg condition, provided that we recognise the surfaces of constant phase of the structure-amplitude pulsations and not the atomic spacings themselves as the reflecting planes responsible for them.

4. Modified Reflection as a Quantum Effect

It is well recognised that the scattering of light with a change of frequency as actually observed is a quantum effect and cannot be explained on the classical dynamics, though there is a classical analogue which agrees with it in certain particulars. The inadequacy of the classical theory is evident even in the case of scattering by individual molecules and becomes clearest when we consider the question of intensities. Taking, for instance, the scattering of light by a hydrogen molecule, the characteristic vibration frequency is 4156 cm.$^{-1}$ in spectroscopic units. Classically, the spectrum of monochromatic light scattered by hydrogen gas should exhibit two spectral lines of equal intensity shifted from the primary radiation in either direction by this frequency. But the intensity of either of the displaced lines on the classical theory would be very small, while in actual fact, this is true only of the line displaced to a higher frequency, whereas the line shifted to a lower frequency is remarkably intense. When we consider light-scattering in crystals, the failure of the classical theory is even more acute. Classically, a crystal if it is an ideally homogeneous solid, should scatter no light at all; in order to explain the observed diffusion of light, we have to postulate that stratifications having the desired frequencies and of specially suitable wavelengths and orientations are present which reflect the incident radiations with a change of frequency. Except for the lowest frequencies of pulsation or at sufficiently high temperatures, thermal agitation would scarcely be adequate to account for the presence of such stratifications. This difficulty disappears when light scattering is regarded as a quantum-mechanical phenomenon, as the production of the stratifications which reflect the radiations would then itself be a part of the process.

In our present X-ray problem, the stratifications with which we are concerned have, in part, a physical basis, namely, the atomic spacings in the crystal, and this fact is responsible for the resulting effects being directed reflections analogous to the Laue spots instead of being a diffuse scattering.

The atomic pulsations which give the periodic variations of structure-amplitude have the same origin as the characteristic internal vibrations revealed in light-scattering or in infra-red absorption, and their frequencies may be so high that the thermal excitation of the same is entirely negligible. Nevertheless, as in the optical case, we should expect them to be excited and give rise to the modified reflection of X-rays even at ordinary temperatures. Further, on the quantum view, such modified reflections should persist without serious diminution of intensity when the crystal is cooled down to low temperatures. *Per contra*, when the crystal is heated, the intensity of the modified reflections should increase but not very greatly until temperatures are reached at which the characteristic vibrations concerned contribute notably to the thermal energy content of the crystal.

As we have already seen, the appearance of the modified reflections in directions other than that of the unmodified ones involves a suitable progression of the phase of the atomic pulsation in the plane of incidence. This "tilting of the wave-fronts" so as to secure the possibility of a Bragg reflection at any arbitrary angle of incidence might seem a very surprising postulate to make when we view the subject classically. But it fits in perfectly with the quantum mechanical point of view according to which the incident radiation itself creates the atomic pulsations which result in its reflection, and the conditions necessary for such reflection are therefore automatically secured. Even on a purely classical view, it is not inevitable that the pulsations in the crystal lattice should be of identical phase everywhere, though the more rigidly constructed the crystal lattice is, the more closely this ideal might be expected to be approached, and the more sharply would the modified reflections be limited to directions approaching that of the unmodified ones.

5. *Analogy with the Compton Effect*

As is well-known, the change of wave-length in X-ray scattering discovered by A. H. Compton in 1922 was explained by him[6] as the result of the transfers of energy and momentum which occur when a photon impinges on a free electron. In the wave-mechanical picture of the same process given by Schrodinger[7] in 1927, the scattering of the photon appears as a reflection of the incident waves by the periodically stratified distribution of charge density obtained on superposing the De Broglie waves of the electron before and after the collision. The Doppler effect due to the movement of these stratifications explains the change of frequency in reflection. That the effect as actually observed is a diffuse scattering follows from the fact that the recoil of a free electron and therefore also the reflection of the incident radiation is in an arbitrary direction. The wave-mechanical picture of the Compton effect is thus rather similar to Brillouin's classical treatment of the

reflection of light by travelling sound-waves. The analogy would be closer still if the stratifications of optical density in the medium were considered as resulting from the incidence of the radiation, as in Schrodinger's treatment, instead of being postulated to exist in advance.

That the change of wave-length in the Compton scattering is a function of the angle of observation follows from the manner of its origin. Several attempts have been made in the past to observe the change of wave-length independent of the angle of scattering which might be expected if the electron which scatters the radiation shifts to a higher energy level while remaining bound to the atom. The theoretical problem has been considered[8] by Sommerfeld in whose note will be found references to various papers in this connection. It is clear that if such an effect exists, the change of wave-length would be much smaller than the Compton shift. Then again, the more firmly the electron is bound to the atom, the less likely it is as the result of the scattering process, to pass to an unoccupied level of higher energy. These circumstances and the necessarily feeble intensity of any effect which appears as a diffuse scattering would militate against its successful detection in experiment. It may be recalled in this connection that the attempts so far made to discover the analogous phenomenon of a change of frequency in light scattering due to the transfer of a bound electron from one energy level to another within an atom have also been unsuccessful.

The preceding discussion prepares us for recognising that the modified reflection of X-rays by crystals and the Compton effect are essentially analogous phenomena, as they both arise from the reflection of radiation by a stratified distribution of electric charge density. There are however also significant differences. In our present case, the electrons remain bound to the crystal lattice of which they form a part, and the stratifications arise from the crystal lattice being set in vibration and causing a periodic variation of the electronic charge density in the crystal structure. Accordingly, in our present case, the resulting effect appears as a directed reflection instead of as a diffuse scattering. The frequency changes in the modified reflection of X-rays are necessarily much smaller than in the Compton effect, indeed so small as to be beyond spectroscopic detection. The differences between the laws of modified and of unmodified reflection of X-rays by crystals should however enable us to recognise their existence.

The analogy between the modified reflection of X-rays and the Compton effect will also be obvious when it is recalled that in the present case as well, the change of frequency and the change in direction of the reflected X-rays may be regarded as a consequence of the exchange of energy and

momentum between the incident quantum of radiation and the crystal lattice. The discussion of this point may however be more suitably undertaken in a later paper in which the intensity problem for modified X-ray reflection will be more fully dealt with.

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REFLECTION OF X-RAYS WITH CHANGE OF FREQUENCY

Part II. The Case of Diamond

By Sir C. V. Raman and Dr. P. Nilakantan

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1. Introduction

We may now proceed to describe the results obtained by using the Laue method with various crystals which demonstrate the phenomenon of modified X-ray reflection and indicate its origin to be that considered in Part I of this paper. The case of diamond is of exceptional interest for various reasons. Its low atomic weight enables it to be used for such studies with comparatively soft X-rays without sensible loss of intensity by absorption within the crystal. Further, as it is an " ideal " crystal having a rigid lattice and a low specific heat, the effect of thermal agitation and of mosaic structure should be negligible. Diamond is therefore specially suitable for the present investigation. The simplicity of its crystal structure also facilitates the interpretation of the observed results.

Thin plates of diamond with their faces parallel to one of the octahedral cleavages of the crystal are readily obtained. The normal to an octahedral cleavage face is an axis of trigonal symmetry, and is inclined to the normals to the other three pairs of octahedral faces at the tetrahedral angle, namely, 109° 28′. Accordingly, if a pencil of X-rays passes through such a plate normal to its faces, it is incident on the three sets of (111) crystal planes at a glancing angle of 19° 28′. The reflections from these planes would therefore appear in the Laue pattern as a distinct group of three spots forming an equilateral triangle which are easily recognised and identified (see Figs. 1 and 2 in Plate XIII). When the crystal setting is not quite normal to the X-ray beam, the triangle appears distorted (see Figs. 3 and 4 in Plate XIV). These photographs were taken with an X-ray tube having a copper anticathode and run at 41000 volts. The beam accordingly contains the Cu K_α and Cu K_β rays in considerable strength, accompanied by white radiations of shorter wave-lengths. When Fig. 1 was photographed the K_β radiations were cut off with a nickel foil, while Figs. 2, 3 and 4 were obtained, with the unfiltered radiation.

2. *Experimental Results*

The four figures exhibit remarkable differences in the appearances of the (111) reflections (three in each figure) produced by varying the angle of incidence and (in Fig. 1) also by cutting off the K_β radiation. The differences consist in the shape, size and intensity of the Laue spots, the appearance of fainter companions in their vicinity, and the presence of streamers radiating at an angle from these companions (see Fig. 3). In order to exhibit clearly how these variations are determined by the glancing angle, eight pictures of the (111) reflections obtained with the unfiltered Cu radiation have been arranged in a vertical row in Fig. 5, Plate XV, so that the positions and intensities of the Laue spot and of its companions can be readily compared by inspection.

To appreciate the significance of the experimental results, we may remark that the (111) planes in diamond are those that give the strongest reflections and have therefore a large structure amplitude. Their spacing is 2·055 A.U. while the effective wave-lengths of the Cu K_α and K_β rays may be taken as 1·537 A.U. and 1·389 A.U. respectively. To obtain a Bragg reflection of the K_α and K_β radiations, therefore, the glancing angles on the (111) planes should be respectively 21° 58′ and 19° 45′. For the series of eight pictures shown in Fig. 5, the actual glancing angle as determined from the position of the Laue spot and the plate distance alters from 17° 10′ for Fig. 5 (*a*) to 22° 13′ for Fig. 5 (*h*), thus covering a range of angles from much below to much above that required for a Bragg reflection of the K_β radiation, while in Fig. 5 (*h*), the glancing angle is nearly that required to give a Bragg reflection for the K_α radiation.

From a study of these photographs, we draw the following conclusions : (1) The companion spots which accompany the Laue reflections appear in the plane of incidence of the X-ray beam on the crystal planes, that is to say, in the same plane as the Laue spots, but unlike the latter, do not satisfy the usual geometrical law of reflection from the crystal planes. (2) The two companion spots are due to the monochromatic Cu K_α and K_β radiations respectively. This is shown by the fact that the inner spot vanishes when the K_β radiation is filtered out. (3) The spots are in the nature of well-defined specular reflections being, in fact, nearly as sharply defined as the usual Laue reflections of the white radiation; they tend, however, to be round instead of elliptic in shape. (4) The intensity of the spots increases rapidly as their position approaches that at which they could be identified with a regular geometric reflection from the crystal planes satisfying the usual Bragg formula. The spots continue to be however of perceptible

intensity for directions removed by at least 10° on either side of such geometric reflection. (5) When a spot is at or near the position of maximum intensity, it is accompanied by streamers which do not lie in the plane of incidence but which appear to stretch towards or away from the two other (111) Laue spots.

The following Table shows the measured distances of the Laue spots and of its two companions in the series of pictures Figs. 5 (*a*) to (*h*) measured from the centre of the Laue diagram, the plate distance being 3·98 cms.

TABLE I

Distances of Spots from Centre

Fig. 5	Laue spot	Inner Companion (K_β)	Outer Companion (K_α)
	Cms.	Cms.	Cms.
(*a*)	2·72	3·13	3·55
(*b*)	2·85	3·20	3·60
(*c*)	3·04	3·22	3·65
(*d*)	3·31	Not separated	3·72
(*e*)	3·38	Not separated	3·74
(*f*)	3·50	3·30	3·76
(*g*)	3·54	3·34	3·78
(*h*)	3·60	3·36	3·81

The distances of a spot from the centre of the pattern for Bragg reflections of the Cu K_α and Cu K_β radiations respectively from the (111) spacings would be respectively 3·83 cms. and 3·28 cms. It will be noticed that these distances coincide with the observed position of the spots when they are near the position of maximum intensity, but tend to deviate systematically from it in one direction or the other when they move away from this position.

3. Interpretation of the Results

The general nature of the results described above leaves little doubt that we are here dealing with modified X-ray reflections of the kind discussed in Part I of the paper. We may however go a little more deeply into the matter in the light of the known crystal structure and properties of diamond.

The (111) planes have the largest spacings and give the strongest reflections amongst the crystal planes in diamond. It is therefore not surprising that they should give the modified X-ray reflections with notable intensity. The reason for this becomes clearer when we examine the nature of these spacings. As is well known, diamond consists of *two* interpenetrating face-centred cubic lattices of carbon atoms which we may refer to as the A and B lattices. The (111) spacings consist of planes of atoms belonging to lattice A interleaved by planes of atoms belonging to lattice B, the distance between the nearest layers of A and B atoms being one-fourth of the distance between the successive planes of A or of B atoms. It is this arrangement that makes the reflection from the (222) planes weak or evanescent, and makes the structure-amplitude of the (111) spacings correspondingly strong. If, now, we imagine the A and B lattices to oscillate as rigid wholes relatively to one another, the structure-amplitude of the (111) spacings should exhibit a strongly marked variation. For, the electron density between the most nearly adjacent A and B planes of atoms would increase when these planes approach each other and *per contra*, diminish when they recede. At the same time, the electron density between the less nearly adjacent A and B planes would behave in the opposite way, that is, would diminish in one case and increase in the other. The oscillation of the two elementary lattices with respect to one another in a direction normal to an octahedral cleavage face should therefore produce a stratification of the electron density which is periodic in time and has the same spacing as the (111) planes. These planes should thus be in a position to give a modified reflection of the incident X-rays.

When a crystal of diamond is illuminated with monochromatic light, the spectrum of the scattered light exhibits a single sharp line of great intensity with a spectral shift of 1332 wave-numbers. It is a well-established result that this frequency-shift is due to the same oscillation which we have considered here, namely, a linear vibration of the two interpenetrating lattices A and B with reference to one another. The oscillation is triply degenerate, in other words, may take place in any arbitrary direction or simultaneously in different directions with arbitrary phases, the frequency being the same in every case. It is evident that the structure-amplitude of a particular (111) spacing would be influenced only if the movement of the lattices has a component normal to that spacing and would be unaffected if the movement is parallel to it. So long, however, as the two interpenetrating lattices move as rigid units and the phase of the motion is identical in all the individual cells, the periodic stratifications of electron density produced by such motion remain everywhere parallel to the respective crystal planes and have identically the same spacing as these planes. On these assumptions, therefore,

the modified reflection of the X-rays by any set of crystal planes would appear only in the same direction as the ordinary Laue reflections.

Actually, as we have seen, the modified X-ray reflections associated with a particular set of the (111) planes in diamond continue to appear with practically undiminished sharpness, though with rapidly diminishing intensity, as we move away from the correct Bragg orientation for the particular X-ray wave-length. Further, as shown by the figures in Table I, if the modified reflection is regarded as a Bragg reflection from a periodic stratification of electron density inclined to the crystal spacing, not only does the effective 'structure-amplitude' of such stratifications diminish rapidly as they are tilted away from the crystal planes, but the effective spacing of such tilted wave-fronts progressively deviates from the actual crystal spacing. A glance at the figures in Table I shows that this apparent change of spacing occurs in such a direction that the modified reflection is nearer to the direction of the Laue reflection than would otherwise be the case. These results become intelligible when we recognize that the circumstances most favourable for the modified reflection to make its appearance are precisely those in which the unmodified reflection is also obtained. In any other case, a modified reflection is only separable from the unmodified reflection if the oscillation of the structure-amplitude departs from the ideal condition of having the same phase everywhere. A diminution of the intensity of the resulting reflection is only to be expected in such circumstances.

Empirically, it is found that the formula

$$\lambda^* \sin(\theta + \phi) = \lambda \cos \phi \qquad (1)$$

nearly fits the results for diamond shown in Table I. Here θ, ϕ are the glancing angles of incidence and reflection with respect to the crystal planes, λ^* is the spacing of the latter, and λ the X-ray wave-length. It will be noticed that the formula is unsymmetrical in θ and ϕ, in other words, they are not interchangeable. On the other hand, a formula of the symmetrical type

$$2\lambda^* \sin \tfrac{1}{2}(\theta + \phi^*) = \lambda \qquad (2)$$

for the modified reflection would make it completely analogous to the Bragg formula and give an angular separation $(\theta + \phi^*)$ of the incident X-ray beam and of the modified reflection which is the same for all orientations of the crystal and therefore identical with that for the unmodified reflection. Comparing (1) and (2), it is easily seen that

$$\text{If } \phi > \theta, \text{ then } \phi < \phi^*$$
$$\text{If } \phi < \theta, \text{ then } \phi > \phi^*$$

This is what the figures given in Table I indicate. Both the formulæ (1) and (2) reduce to the Bragg formula when $\theta = \phi$ or ϕ^*.

We may now remark on the explanation of the oblique streamers [seen in Fig. 3 and Fig. 5 (*h*)] which as already mentioned, accompany the modified X-ray reflection in diamond when it is of sufficient intensity. It will be noticed that they radiate towards or away from the two other Laue spots due to the (111) spacings, instead of towards the centre of the pattern. Their explanation is to be found in the fact already remarked that the lattice oscillation in diamond is triply degenerate, and may therefore co-exist in different directions and in different phases. In general, therefore, variations of the structure factor of each of the three sets of (111) planes would occur simultaneously. An X-ray beam incident on any one set of these planes and reflected by it would also be influenced by the stratifications having the same spacing and frequency parallel to the two other sets of these planes. The streamers accompanying the modified reflection are evidently secondary effects due to the superposition of the three sets of stratifications. This is clearly shown by the directions which they assume.

The radial streamers which stretch from the Laue reflections towards the centre of the pattern have a different origin. They are best seen with diamond when the modified reflections due to the K_α and K_β rays both lie outside the Laue spot, and may therefore be identified with the modified reflection of the *white* radiations of shorter wave-lengths present in the incident X-ray beam.

4. *Significance of the Diffuse Halo*

Referring again to Figs. 1, 2, 3 and 4 in the Plates, a very striking feature of these Laue patterns is the strong though diffuse halo which appears surrounding the primary X-ray beam. Its outer limit is ill-defined, and indeed towards its periphery the halo mingles insensibly with the diffuse scattering by the crystal which overlays the entire Laue pattern. It is, however, evident that the intensity of the halo is relatively great over a limited area which lies well within the triangle formed by the (111) Laue spots. That the phenomenon is really due to the diamond has been fully established by blank exposures without the crystal which give a clear film except over a narrow ring due to the primary beam surrounding the blocked-out circle at the centre. Allowing for this narrow ring, it appears that the maximum intensity of the halo is not at the centre of the pattern, but very definitely further out, in fact about half-way between the centre and the (111) Laue spots. In well-exposed pictures, the falling off in the intensity of the halo towards its centre is clearly seen. In considering the origin of the halo, we

must, of course, take into account the composition of the incident X-radiations, which includes besides the Cu K_α and K_β rays, also a considerable intensity of white radiation of shorter wave-lengths. The elimination of the latter, if it had been possible, would undoubtedly have accentuated the falling off in intensity of the halo towards the centre of the pattern and made the existence of a well-defined maximum at a distance from the centre more strikingly evident. There can be little doubt, however, that the most intense region of the halo owes its origin to the monochromatic K_α and K_β radiations of the copper anticathode.

It will be remembered that in Part I of the paper, we have referred to Brillouin's theory of the reflection of monochromatic X-rays by sound-waves of thermal origin. This theory indicates the appearance of a continuous diffusion halo in the X-ray pattern extending from the centre outwards and falling off in intensity to zero at an angle corresponding to the short wave-length limit of the acoustic spectrum. Brillouin's expression for the intensity of the halo includes a Planck factor which is equal to unity for the lowest frequencies and tends to zero for acoustic frequencies for which $h\nu \gg KT$. Accordingly, for the case of diamond, the intensity of the Brillouin halo should be vanishingly small except very near its centre. Actually, as is evident from the photographs, the halo is a conspicuous phenomenon and exhibits a maximum at an angular radius from the centre of about 20°. It is therefore clear that though the halo is evidently due to the reflection of the X-rays by acoustic waves as postulated by Brillouin, its intensity is much larger than that indicated by his theory. The basic idea of his theory, namely, that the sound-waves responsible for the scattering of X-rays are of thermal origin, cannot therefore be accepted. If, however, we consider the acoustic waves to be actually excited by the X-ray quanta, the difficulty would disappear, as the intensity of the scattering would then be vastly greater and in better accord with the observed facts. The distinct concentration of the scattering in a ring-shaped halo sugests that the acoustic spectrum has a marked intensity maximum at a wave-length roughly about double the shortest permissible.

We must not, of course, omit to mention the Compton scattering. Theory indicates that this is of zero intensity for the forward scattering and increases to its full value at large angles. In the case of diamond, the Compton scattering is probably responsible for most of the radiation diffused by the crystal through large angles. Nearer the centre of the pattern, however where the intense diffuse halo is observed, the Compton scattering is less important, and the observed effect is mostly due, as we have seen, to the acoustic waves excited by the incidence of the X-radiation.

5. *Influence of Temperature*

As explained earlier in the paper, the choice fell on diamond as the crystal for these experiments, mainly because phenomena of purely thermal origin would, *prima facie*, be negligible in dealing with it. This is evident when we consider the magnitude of the Planck factor $1/(e^{h\nu/KT}-1)$ which indicates the extent of thermal excitation of any oscillation of frequency ν. At room temperature ($\tau = 300°$), $h\nu = KT$ for a frequency $\simeq 6 \times 10^{12}$, whereas the characteristic frequency of diamond corresponding to 1332 cm.$^{-1}$ is 40×10^{12}. The magnitude of the Planck factor for this frequency is entirely negligible, while it is small even for a frequency which is only half of it. The appearance of a modified X-ray reflection due to the lattice oscillation in diamond and indeed also of the scattering by the acoustic waves for lower frequency must therefore be regarded as quantum effects. A very convincing demonstration that this is the case would be to cool down the diamond to liquid air temperatures and to observe whether the effects under consideration persist undiminished, as is to be expected. Experiments of this kind are in progress and will be reported as soon as they are completed. As corresponding experiments with light show that modified scattering persists with undiminished intensity at the lowest temperatures, we may confidently anticipate an analogous result also with modified X-ray reflection at angles close to the usual Laue reflections. The falling off in the intensity of the modified reflection when the crystal is tilted away from the correct position for a Bragg reflection may however conceivably show a more marked temperature dependence. This is a matter for further investigation.

In the case of the modified scattering of light, the intensities of the Stokes and anti-Stokes components are respectively proportional to $1/(1-e^{-h\nu/KT})$ and $1/(e^{h\nu/KT}-1)$. The first of these quantities is approximately independent of temperature so long as $h\nu \gg KT$. For a characteristic frequency 40×10^{12}, the temperature dependence of the intensity of the Stokes component should only become sensible when $T > 1000°$. Investigations on light scattering in diamond made recently at Bangalore show that when the crystal is heated, it exhibits an appreciable alteration of the characteristic frequency, and it is probable also that at higher temperatures the frequency broadens out into a band. Accordingly, we should not be surprised to find in the X-ray phenomena temperature effects more pronounced than those indicated by the formula quoted.

Photographs of the Laue pattern of diamond at 25° C. and at 500° C. show at the higher temperature a slight enfeeblement of the ordinary Laue reflections, and a detectable but not very striking enhancement of the

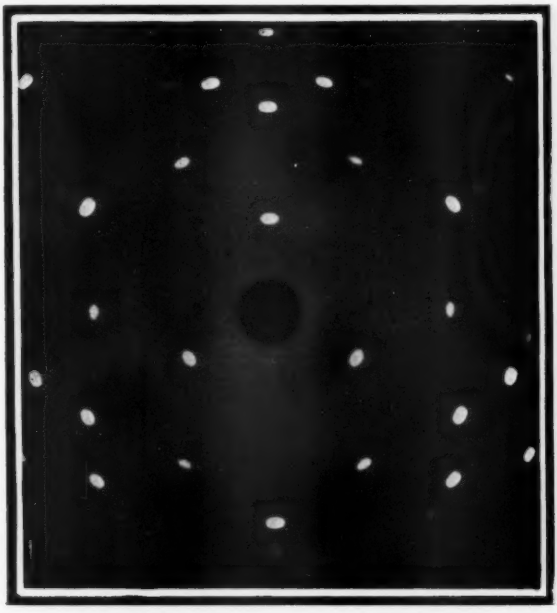


FIG. 1 — Filtered, Cu Kα Radiation only

FIG. 2 — Unfiltered, Cu Kα & Cu Kβ Radiation

Symmetrical Laue Pattern of Diamond
(normal to cleavage plane)

Fig. 3

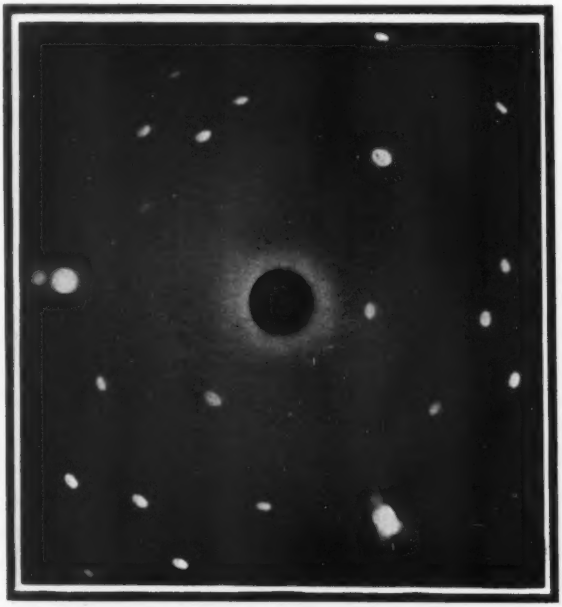
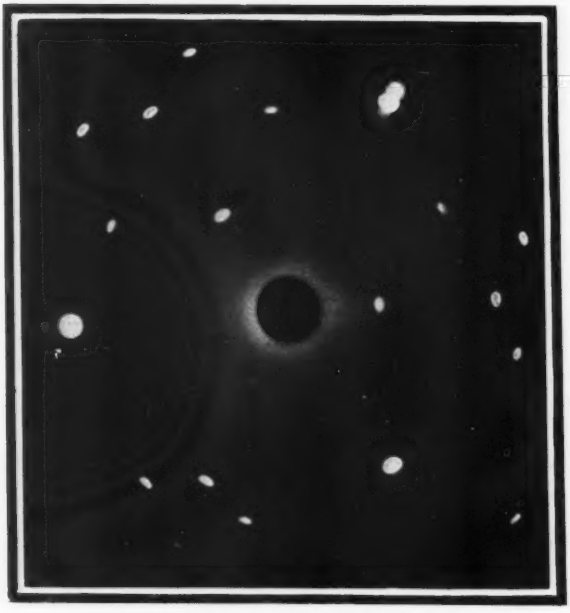


Fig. 4



Asymmetrical Laue Pattern of Diamond
(approximately normal to cleavage plane)

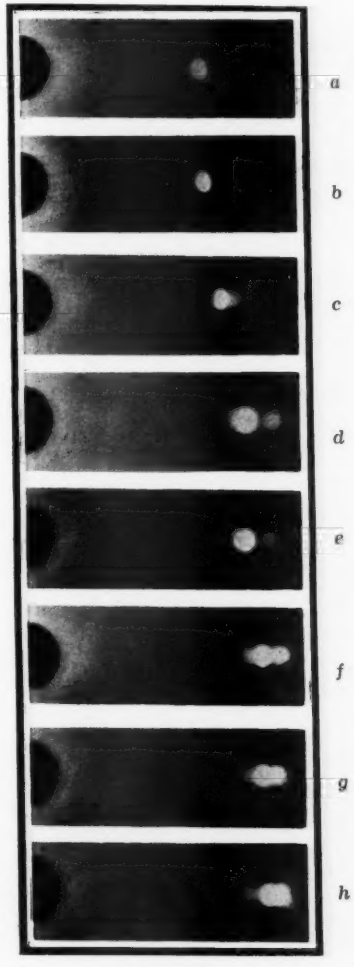


FIG. 5

Showing Laue Spot due to Reflection from [111] Planes of Diamond and Modified Reflections due to Kα and Kβ Radiations

intensity of the modified reflections, as also of the diffuse halo appearing in the pattern. The thermal expansion of the crystal with consequent shifting of the relative positions of the Laue and modified reflections however complicates the issue, as the intensity of the modified reflections depends greatly on their relative position. A more detailed study is therefore necessary before any definite conclusions can be drawn. Nevertheless, the observations so far as they go indicate pretty clearly that the modified reflection of X-rays and the diffuse halo are not *primarily* thermal phenomena. This statement, it will be noticed, does not exclude observable thermal influences on the phenomena, such as a sharpening of the reflections at low temperatures, or their brightening up and becoming more diffuse at high temperatures.

REFLECTION OF X-RAYS WITH CHANGE OF FREQUENCY

Part III. The Case of Sodium Nitrate

By Sir C. V. Raman and Dr. P. Nilakantan
(*From the Department of Physics, Indian Institute of Science, Bangalore*)

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1. Introduction

Sodium nitrate is very similar in crystalline form and structure to calcite, but owing to the lower atomic weight of sodium, is better suited than calcite for X-ray studies with a copper-target tube. Its physical properties present a striking contrast with those of diamond. The melting point of the crystal is 309·5° C., indicating that its characteristic frequencies are low. The unit cell contains two ions of Na and two of NO_3 situated along the trigonal axis of symmetry. There are thus ten atoms in the cell occupying non-equivalent positions, and the possible modes of oscillation of the interpenetrating lattices are therefore numerous. Theory indicates that there should be eighteen fundamental frequencies of vibration, nine of them being doubly degenerate. Ten of these fundamentals should have low frequencies representing translatory movements of the Na and NO_3 ions and rotational oscillations of the latter. The remaining eight fundamentals should have high frequencies corresponding to the internal vibrations of the NO_3 ions. Actually, the crystal exhibits two low and three high frequencies in light-scattering, while in infra-red absorption, three low and three high frequencies have been observed, all these being different. Three low and two high frequencies are theoretically forbidden from appearing either in light-scattering or in infra-red absorption. The agreement with theory is thus nearly complete. Diagrams illustrating the different possible modes of oscillation will be found in a recent paper by Bhagavantam and Venkatarayudu (1939). Nedungadi (1939*a*) has studied in considerable detail, the influence of temperature on the spectrum of light-scattering in sodium nitrate, and has found that the two low frequency lines with wave-number shifts 98 and 185 are displaced to still lower frequencies and broaden greatly when the crystal is heated above 180° C., finally becoming diffuse bands as the melting point is approached. Nedungadi (1939*b*) has also identified the modes of vibration corresponding to these low frequencies by studies of the polarisation of light-scattering in orientated crystals.

The planes in the crystal structure parallel to the rhombohedral cleavages give by far the most intense X-ray reflections. As in the case of diamond, therefore, we should expect these planes also to give intense modified reflections. The diagonal planes passing through the edges of the cleavage rhomb and bisecting the acute angle between its faces also give intense Bragg reflections, and by the same token should give strong modified reflections. The crystal planes normal to the trigonal axis of symmetry consist of alternate layers of Na and NO_3 ions. The reflections due to these planes are not very strong. In view, however, of the fact that several of the fundamental modes of vibration consist of movements of the Na and NO_3 ions along the axis of symmetry, marked variations of the structure-amplitude of these planes may be expected. We may therefore reasonably anticipate that these planes should give modified reflections with notable intensity.

Remarkable changes are observed in the intensity of the rings in the X-ray powder pattern of sodium nitrate when the temperature is raised above 180° C. and up to a little below its melting point. These changes have been very fully studied by Kracek and co-workers (1931), whose results have been confirmed by Nedungadi at this Institute. The most interesting feature is that above 180° C., the rise of temperature affects the intensity of the X-ray reflections due to different spacings very unequally. Some are scarcely affected, some reflections diminish in intensity a little, while a few which are fairly strong below 180° C. are practically wiped out when the temperature rises towards 250° C. It thus appears that the structure-amplitude of some of the spacings is very markedly a function of temperature in this range. Kracek and his co-workers have suggested that this is due to the rotational oscillations of the NO_3 ions gradually increasing in amplitude and passing into continuous rotation in the temperature range from 180° C. to 290° C. It may be mentioned that this is also the temperature range in which Nedungadi finds that the low frequency lines observed in light scattering broaden out and shift to lower frequencies.

To bring out the position clearly, we give below in Table I, a list of the principal planes and crystal spacings in sodium nitrate, and the intensities of the X-ray reflections due to them (on an arbitrary scale) as given by Kracek *et al.*, at 25° C. and at 280° C.

The Millerian indices of the planes given in the first column of the table have reference to the axes of the elongated rhombohedron which is the unit cell of the crystal lattice. In this notation, (211) represents a cleavage face, (323) is a diagonal plane bisecting the acute angle between the cleavage faces and (222) is normal to the trigonal axis. It will be noticed from the table

TABLE I

Crystal Spacings in Sodium Nitrate

Indices	Spacing Å. at 25° C.	Spacing Å. at 280° C.	Intensity at 25° C.	Intensity at 275° C.	Structure-Amplitude
110	3·902	3·921	2	3	N + O − Na
211	3·035	3·121	> 10	> 10	N + O + Na
222	2·802	2·932	4	2·5	N + O − Na
$1\bar{1}0$	2·534	2·543	3	3·4	N + O + Na
210	2·310	2·313 at 250° C.	6	< 0·5	O
200	2·122	2·138	4	2·4	N + O − Na
220	1·943	1·964	1	7·7	N + O + Na
323	1·893		7		N + O + Na
321	1·880	1·914	3	2·2	N + O − Na
$2\bar{1}0$	1·649	..	3	< 0·5	O
$2\bar{1}1$	1·626	1·637	2	1·2	N + O − Na

that the (211) and (323) planes give strong reflections which are scarcely influenced by temperature, while the (222) planes give a weaker reflection which falls off appreciably on heating. The (210) planes are specially remarkable as they give a strong reflection which disappears at high temperatures. The last column in the table indicates the manner in which the structure-amplitude of the respective planes is effectively determined by the contributions of the three species of atoms in the crystal, according to Kracek and his co-workers.

2. *Experimental Results*

Figs. 6 and 7 in Plate XVI, Figs. 8 and 9 in Plate XVII, Figs. 10 and 11 in Plate XVIII, Figs. 12 and 13 in Plate XIX, Figs. 14 and 15 in Plate XX are Laue patterns of sodium nitrate obtained with the unfiltered radiation from a copper target. They illustrate the phenomena exhibited by this crystal in various circumstances. Figs. 6, 7, 8, 9, 10 and 11 show the modified reflections by some of the principal planes at various angles of incidence, while Figs. 12, 13, 14 and 15 exhibit the effect of raising the temperature from 25°C. successively to 200°, 225° and 275° C., the position of the crystal remaining unaltered.

In obtaining all these photographs, the crystal was placed with one of its cleavage faces in a vertical plane, the longer diagonal of this face being vertical. The incident X-ray beam passsed through the cleavage face in a horizontal direction, and its angle of incidence on the various crystal planes could be altered by rotating the crystal about the vertical diagonal. In all the settings of the crystal, the trigonal axis of the crystal remained horizontal, its inclination to the X-ray beam being varied. The Laue patterns accordingly exhibit two-fold symmetry about a horizontal axis. The two other cleavage faces of the crystal being inclined to the vertical, the reflections from them appear in two directions symmetrically inclined to the horizontal. The (222) and (323) planes being always vertical, the reflections from them appear on the horizontal axis of the pattern in suitable settings of the crystal.

The most conspicuous features in Figs. 6, 7, 8 and 9 besides the usual Laue spots, are the modified reflections from the two cleavage planes. In Figs. 7 and 8, the K_α and K_β modified reflections appear as distinct spots adjacent to the Laue reflections from the same planes, while the modified reflections of the white radiation appear as radial streaks stretching towards the centre of the pattern and distinctly separated from the K_α and K_β reflections. In Figs. 6 and 9, the Laue reflections are far removed from the modified reflections of the K_α and K_β rays in one direction or the other; but the latter continue to be visible in approximately the same positions as in Figs. 7 and 8, though only as diffuse spots or clouds. The radial streaks are also seen in approximately the same positions. That the latter are due to the modified reflection of the white radiation will be very evident on comparing Figs. 6 and 9. When the Laue spots are nearer the centre of the pattern than the modified reflections of the K_α and K_β radiations, they are traversed by the radial streaks, whereas when the Laue spots are further away, they are not overlaid by the streaks.

The inclination of the X-ray beam to the trigonal axis of the crystal in Figs. 6, 7, 8 and 9 was successively 56°, 50°, 44° and 39°. It is a notable fact that the modified reflections from the cleavage planes continue to be visible in spite of the large change in the angle of incidence which is indicated by the displacement of the Laue reflection from near the centre of the photograph to near its outer margin. On comparing Figs. 7 and 8, the great increase in the intensity of the modified reflection of the K_α radiation when it approaches the Laue spot will be evident. This phenomenon has already been noted in the case of diamond. It is evident, however, that the modified reflections are more conspicuous in intensity and observable over a wider range of incidences in sodium nitrate than in diamond. They are also somewhat more diffuse than is the case with diamond.

In obtaining the Laue patterns reproduced as Figs. 10 and 11, the crystal was turned over by 180° about the vertical diagonal. This made it possible to get the reflections from the (222) planes to the left of the pattern simultaneously with those from the (211) and the (323) planes on its right. A slightly smaller plate distance was also used. The modified reflection of the K_α radiation from the (222) planes is clearly seen in Figs. 10 and 11 to the right and left of the Laue spots respectively, the actual glancing angle of the beam on this plane in the two photographs being 18° and 11°, being thus respectively greater and less than the Bragg angle of 15° 55′. The spacing of the (323) planes being 1·893 A., the Bragg angle for these planes and the K_α radiation is 23° 57′. This being much greater than the actual glancing angle in either of the two patterns, we do not observe the modified reflection of the K_α and K_β radiations from the (323) planes but only those of the white radiations of shorter wave-length. These appear as intense horizontal streaks passing through the Laue reflections. It is obvious that the modified reflection of monochromatic rays by a particular set of crystal planes cannot be observed if the wave-length of the rays used is too great to give a Bragg reflection, or if the glancing angle differs too largely from that required for such reflection. In such cases, however, if the white radiation present in the X-ray beam is sufficiently intense, its modified reflection may be observed as a radial streak passing through the Laue spot. Numerous examples of this may be seen in the photographs reproduced.

3. Geometry of Modified Reflection

In Part II of the paper, it was mentioned that an empirical formula of an unsymmetrical type fitted the observations with diamond, namely,

$$d \sin (\theta + \phi) = \lambda \cos \phi \qquad (1)$$

θ and ϕ being the glancing angles of incidence and of modified reflection and d the crystal spacing. An alternative formula was also given which is symmetrical in θ and ϕ, namely,

$$2 d \sin \tfrac{1}{2} (\theta + \phi) = \lambda \qquad (2)$$

This formula would have a theoretical basis if it be assumed that as the wave-fronts of the stratification giving the modified reflections tilt round, they maintain the same spacing as the crystal planes of which they are the structure-amplitude fluctuations. In Table II are collected the values of θ and ϕ as given by the observed positions of the Laue spot and of the modified reflection, the spacing d as calculated from formulæ (1) and (2), and as known from the crystal structure. The data refer to the crystal at room temperature.

TABLE II

Modified Reflections by Sodium Nitrate
(211) *Planes : Crystal Spacing* = 3·035 *A. U.*
(*The symbol* α *indicates* K_α *reflection ;* β *indicates* K_β *reflection*)

Character of Reflection	Glancing Angle		Spacing calculated from Formula (1) in A.U.	Spacing calculated from Formula (2) in A.U.
	Incidence θ	Reflection ϕ		
Very Diffuse	5° 24′	23° 44′α	2·896	3·060
,,	6° 20′	22° 48′α	2·942	3·090
,,	6° 44′	22° 26′α	2·920	3·056
,,	7° 48′	21° 22′α	2·944	3·056
Diffuse	10° 27′	18° 58′α	2·966	3·029
		15° 33′β	3·055	3·031
,,	11° 34′	17° 46′α	2·994	3·040
		14° 57′β	3·007	3·092
Fairly Sharp	11° 6′	18° 19′α	2·975	3·029
		15° 22′β	3·007	3·035
,,	11° 50′	17° 20′α	3·016	3·056
		14° 38′β	3·017	3·035
Sharp	15° 52′	13° 28′α	3·057	3·040
		10° 36′β	3·064	3·035
,,	15° 58′	13° 17′α	3·065	3·046
		10° 20′β	3·084	3·054
Very Diffuse	19° 58′	9° 12′α	3·085	3·022
,,	20° 47′	8° 23′α	3·092	3·022

Tables II and III include the data for the modified reflections observed in all the six Laue patterns and the corresponding spacings. It is clear from the figures that the experimental results for sodium nitrate fit the symmetrical formula (2) very well, and that the unsymmetrical formula (1) is not applicable in the case of this crystal. The figures for the (111) spacing in diamond given in Part II are compiled in Table IV in the same way as for sodium nitrate. It is clear that the experimental data for diamond agree

TABLE III

Modified Reflections by Sodium Nitrate

Glancing Angle		Spacing calculated from Formula (1) in A.U.	Spacing calculated from Formula (2) in A.U.
Incidence θ	Reflection ϕ		
(222) *Planes*: *Crystal Spacing* = 2·802 *A.U.*			
11° 50′	20° 48′α	2·669	2·739
	17° 29′β	2·707	2·740
18° 29′	14° 1′α	2·779	2·750
	10° 50′β	2·787	2·740
(210) *Planes*: *Crystal Spacing* = 2·310 *A.U.*			
18° 12′	20° 29′α	2·307	2·325
	16° 41′β	2·327	2·317
19° 17′	19° 57′α	2·289	2·292
	15° 36′β	2·349	2·317
(200) *Planes*: *Crystal Spacing* = 2·122 *A.U.*			
21° 51′	20° 27′α	2·144	2·132
22° 31′	20° 8′α	2·133	2·115

better with the unsymmetrical formula (1) though even here there is a systematic deviation. The symmetrical formula (2) is evidently inapplicable in the case of diamond.

It is remarkable that the geometric law of the modified reflections should differ so markedly with the two different crystals. It is, of course, not possible to generalise on the evidence of these two cases only. But it is permissible to suggest that these and other differences already noticed between the cases of diamond and sodium nitrate are connected with the great difference in their crystal structure and properties, and especially with the fact that diamond has a very high characteristic frequency, while sodium nitrate has numerous low frequencies and is therefore influenced to a far greater extent by thermal agitation. There is also the possibility that there may be a difference in the behaviour of "ideal" crystals and of those with a "mosaic structure". Diamond almost certainly belongs to the first class, and sodium nitrate probably to the second. The pulsations of structure-amplitude could scarcely

TABLE IV

Modified Reflections by Diamond
(111) *Planes*: *Crystal Spacing* = 2·056 *A.U.*
(*The symbol* α *indicates* K_α *reflection ;* β *indicates* K_β *reflection*)

Glancing Angle		Spacing calculated from Formula (1) in A.U.	Spacing calculated from Formula (2) in A.U.
Incidence θ	Reflection ϕ		
17° 11′	24° 33′α	2·104	2·161
	21° 0′β	2·098	2·123
17° 48′	24° 24′α	2·086	2·142
	21° 0′β	2·070	2·091
18° 41′	23° 50′α	2·084	2·122
	20° 18′β	2·071	2·081
19° 53′	23° 12′α	2·070	2·094
20° 10′	23° 2′α	2·069	2·090
20° 40′	22° 43′α	2·067	2·080
20° 49′	22° 43′α	2·062	2·073
	19° 11′β	2·041	2·031
21° 4′	22° 41 α	2·052	2·065
	19° 6′β	2·034	2·023

be expected to be coherent as between consecutive units in a "mosaic" structure, while in an ideal crystal, a strict coherence of phase might well be possible. Until the intensity problem for the modified reflection of X-rays is fully worked out, however, it would be premature to discuss the probable influence of mosaic structure on the results.

4. *Influence of Temperature*

The series of four photographs (Figs. 12, 13, 14 and 15) reproduced in Plates XIX and XX exhibit the effect of heating the crystal from 25° C. to 200° C., 225° C. and 275° C. respectively. It will be noticed that as the crystal is heated, the separation between the Laue and K_α modified reflections diminishes, until at 275° C. they are superposed on each other. This naturally involves a large increase in the intensity of the modified reflections of both the

K_α and K_β radiations. Apart from this incidental circumstance which is due to thermal expansion, we notice the following interesting effects :—

(1) There is a marked increase in the intensity of the modified reflection of the white radiation from all the planes in the crystal, including the (211) planes.

(2) While there is a distinct diminution in the intensity of all the Laue spots, the changes in their *relative intensity* are extremely conspicuous. Indeed, on a careful comparison, it will be seen that some spots which are larger and brighter than others at 25° C. have become much feebler or almost disappeared at 275° C.

(3) Fig. 15 shows four *faint* Laue spots which are accompanied by *strong* modified reflections, while in Fig. 12, the same Laue spots are intense but the modified reflections are invisible. Figs. 13 and 14 show a progressive *diminution* in the intensity of these Laue spots and a progressive *increase* in the intensity of the modified reflections accompanying them. These spots have been identified from their positions as due to the (210) planes.

On a reference to Table I, it will be noticed that the (210) planes give strong Bragg reflections at 25° C., but the intensity of these reflections falls to a very small value at 280° C. We have thus *the very interesting result that the planes of which the structure-amplitude falls to zero with rising temperatures show simultaneously a large increase in the intensity of the modified reflection.*

So far from being surprising, these results are entirely in accord with the general ideas developed in Part I. The variations of structure-amplitude produced by the lattice vibrations determine the intensity of the modified reflections. In the limiting case when the thermal agitation is negligible, the lattice oscillations are themselves to be regarded as excited by the incident radiation, the modified reflection being then a pure quantum effect. With rise of temperature, however, the thermal excitation of the lattice vibrations begins to assume importance, especially when, as in the case of sodium nitrate, these are of sufficiently low frequency. The dynamic part of the structure-amplitudes would increase progressively and even rapidly, and the intensity of the modified reflection would show a corresponding increase. It must be remembered in this connection that the static and dynamic structure-amplitudes cannot be regarded as completely independent of each other. For an infinitesimal disturbance of the lattice it might be correct to regard the dynamic variation of the structure-amplitude as superposed on the static structure-amplitude without sensibly influencing it. This would however cease to be true when the amplitudes of vibration are finite. The actual influence of the

vibration on the static structure-amplitude would naturally depend on the circumstances of each case. Broadly speaking, however, it may be said that with increasing amplitude of vibration, the static structure-amplitudes would diminish and the dynamic amplitudes would increase, the two effects being closely correlated. In other words, with rise of temperature, the unmodified or Laue reflections would diminish in intensity, and the modified reflections would correspondingly become more intense. It is thus clear that the modified reflection of X-rays plays a very important role in the theory of the temperature effect in X-ray diffraction. This is particularly well brought out by the case of the (210) planes in sodium nitrate which, as we have seen, show a static structure-amplitude tending to zero with rise of temperature and a dynamic structure-amplitude rising to a correspondingly high value.

Summary of Parts I, II and III

These papers deal with a new type of X-ray reflection in crystals which is dynamic in character and thus differs from the static reflections of the Laue type.

Part I considers the broad theoretical aspects. The optical analogy of the scattering of light in crystals indicates that when X-rays traverse a crystal they excite pulsations in the crystal lattice having the characteristic infra-red frequencies, and these pulsations in turn cause periodic variations in the structure-amplitude of the crystal spacings and therefore result in reflections of the X-rays with change of frequency. At the Bragg angle of incidence, the modified and unmodified reflections are superposed, but when the incidence is increased or decreased, the unmodified reflections disappear, thus enabling the modified reflections to be observed by themselves. They are seen in the plane of incidence on the crystal spacing, but at an angle greater or less than that of geometric reflection by the crystal planes. The modified reflection is a quantum effect and is not primarily a thermal phenomenon, though for low lattice frequencies or at high temperatures it may be thermally influenced.

Part II describes the experimental results obtained by the study of the modified reflection from the (111) planes in diamond. The lattice vibration which is effective is that characteristic of the crystal which also appears in light-scattering with a frequency of 1332 cm.$^{-1}$. This is confirmed by the character of the effects as described in detail.

Diamond exhibits a diffuse halo with a distinct darkening at the centre of the pattern and a maximum of intensity at a distance from it. This is explained as due to acoustic waves of high frequency excited by the incident monochromatic X-rays and reflecting them in the usual way.

Part III describes the results obtained with sodium nitrate which exhibits intense modified reflection by several of the crystal spacings. The geometric law of modified reflection is discussed in relation to the experimental data for both crystals. A study of the temperature effects observed with sodium nitrate indicates that a diminution in the intensity of the unmodified reflection is accompanied by an increase in the intensity of the modified reflection. The modified reflections therefore play an important point in the theory of the temperature effect in X-ray diffraction.

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FIG. 6 — X-ray beam inclined 56° to the trigonal axis

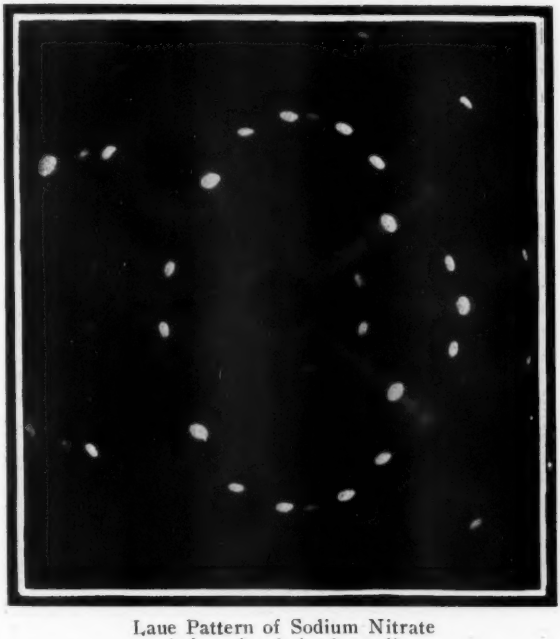

FIG. 7 — X-ray beam inclined 50° to the trigonal axis

Laue Pattern of Sodium Nitrate
(trigonal axis horizontal)

FIG. 8 X-ray beam inclined 44° to the trigonal axis

FIG. 9 X-ray beam inclined 39° to the trigonal axis

Laue Pattern of Sodium Nitrate (trigonal axis horizontal)

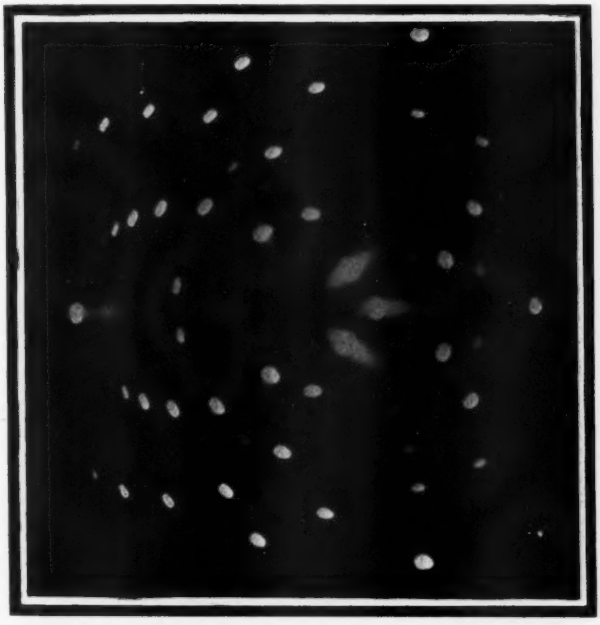

Fig. 10 — X-ray beam inclined 18° to [222] Planes

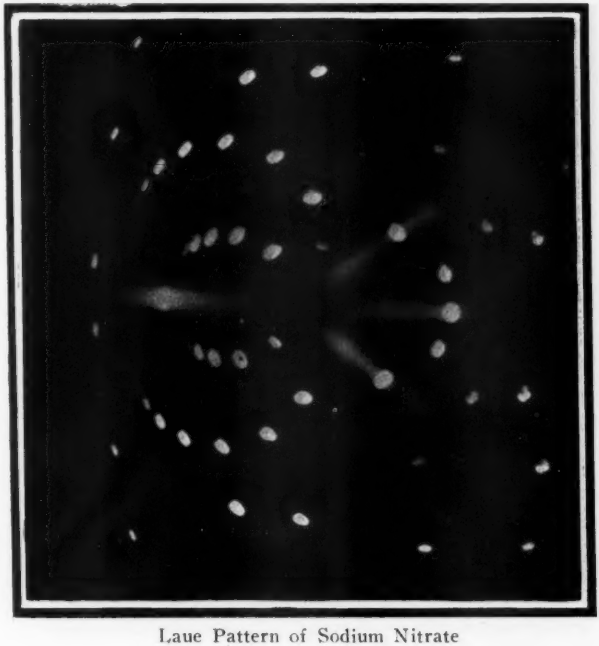

Fig. 11 — X-ray beam inclined 11° to [222] Planes

Laue Pattern of Sodium Nitrate

FIG. 12 — 25°C.

FIG. 13 — 200°C.

Temperature Studies with Sodium Nitrate
(X-rays perpendicular to one of the cleavage faces)

FIG. 14 225° C.

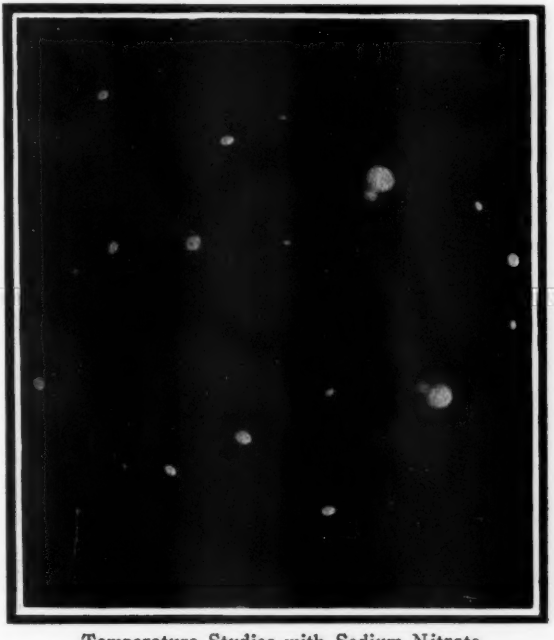

FIG. 15 275° C.

Temperature Studies with Sodium Nitrate
(X-rays perpendicular to one of the cleavage faces)

SYNTHESES IN THE CHAULMOOGRIC ACID SERIES

Part II. Synthesis of Δ^2-Cyclopentene Carboxylic Acid

By K. V. Bokil and K. S. Nargund.

(From the Chemical Laboratory, M. R. Science Institute, Gujarat College, Ahmedabad)

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(Communicated by Dr. K. R. Krishnaswami)

In Part I of this series Bokil and Nargund (1937) described the synthesis of dihydrohydnocarpic acid and indicated a method for the synthesis of hydnocarpic acid and its lower homologues. Recently Cole and Cordoso (1939) published a paper in which they claim to have isolated the whole series of even numbered lower homologues of chaulmoogric acid, excepting one—$C_8H_{12}O_2$—which they could not isolate, although they stated that they obtained an indication of its presence in the mixture of acids from Hydnocarpus Wightiania. Thus, in addition to hydnocarpic acid (C_{16}) they obtained (1) Alepric acid—($C_{14}H_{24}O_2$), (2) Aleprylic acid—($C_{12}H_{20}O_2$), (3) Aleprestic acid—($C_{10}H_{16}O_2$), and (4) Aleprolic acid—($C_6H_8O_2$)—the last two in an impure condition.

The present authors were already engaged in the synthesis of the acids —$C_6H_8O_2$-and-$C_8H_{12}O_2$— along with hydnocarpic acid. Now that the American authors report the isolation of Aleprolic acid (impure) it is proposed to give the synthesis of the same, carried out on the lines indicated in Part I.

Ethyl cyclopentanone carboxylate was reduced according to the method of Dieckmann (1901). The dehydration of the resulting hydroxy ester by phosphorus pentoxide in benzene gave a mixture of Δ^1 and Δ^2 unsaturated esters. By analysis according to the method of Linstead and May (1927), it was found that the mixture contained 82 per cent. of the Δ^2-ester. The mixture was hydrolysed in the cold to the corresponding mixture of acids from which, after distillation, some solid separated on cooling. This solid —(more of which was obtained later during the purification of the Δ^2-acid) was identified as Δ^1-cyclopontene carboxylic acid (m.p. 123–24°) as it was identical with the one obtained from cyclopentenyl cyanide (Nandi, 1934) by alkali hydrolysis. Dieckmann (*loc. cit.*) had already prepared this acid by heating the corresponding hydroxy acid and gave the m.p. as 120°. The liquid left after separating the above acid was partially esterified (5 hours) using the quantities recommended by Linstead, Kon and Maclenan (1932). The ester recovered was still impure as indicated by iodine number (Hanus)

determined under new and more suitable conditions than those usually employed (*vide* experimental). The ester was, therefore, hydrolysed and the acid again partially re-esterified (3 hours). The pure ethyl Δ^2-cyclopentenyl carboxylate, thus obtained, was again hydrolysed in cold to get pure Δ^2-cyclopentenyl carboxylic acid—the inactive Aleprolic acid of Cole and Cordoso (*loc. cit.*).

The iodine value (Hanus)—even under the new conditions—of Δ^2-cyclopentenyl carboxylic acid was only 179·3,—the theoretical value being 222·7 ! The iodine value (J) determined according to Linstead and May's method was also low—*viz.*, 22·7 ! These low iodine values have been found to be due to the instability of the iodine addition product as indicated by the instantaneous separation of iodine at the end during titration with thiosulphate solution.

By a suitable modification of the above method we have now been able to synthesise hydnocarpic acid and the acid—$C_8H_{12}O_2$—the details of which will be published in due course.

Experimental

Dehydration of ethyl-2-hydroxy cyclopentane carboxylate.—The hydroxy ester (25 gms.) P_2O_5 (27 gms.) and benzene (75 gms.) were refluxed together on water-bath for 3 hours. Water was then added, the benzene layer separated, washed with sodium carbonate solution and water, dried over calcium chloride, benzene removed and the residue distilled under reduced pressure. Yield—11 gms ; b.p. 70–80° at 10–12 mm. It had $D_4^{27} = 0 \cdot 9844$ and $N_D^{27} = 1 \cdot 44886$ and iodine value = 72·24 (according to the method of Linstead and May).

Isolation of Δ^1*-acid.*—The above ester was hydrolysed in cold with ten per cent. methyl alcoholic potassium hydroxide (slight excess). The excess alkali was neutralised, methyl alcohol removed under reduced pressure, acidified with dilute sulphuric acid, extracted with ether, dried over anhydrous sodium sulphate and the substance recovered distilled under reduced pressure (yield—8·5 gms, b.p. 104° at 5 mm.). A solid (0·2 gms.) separated on standing. It was freed from the liquid and, on crystallisation from dilute alcohol, had m.p. 123–24°. For purposes of identification Δ^1-cyclopentenyl cyanide (Nandi, *loc. cit.*) was hydrolysed by boiling with alkali and the acid obtained cyrstallised in long feathery plates, m.p. 123–24°, and did not depress the m.p. of the above product. (Found : C, 64·3, H, 7·2 per cent.; Eqt.-wt., −111·8. $C_8H_6O_2$, requires C, 64·3; H, 7·1 per cent., Eqt-wt., 112) Iodine value = 2·2 (according to Linstead and May's method). It was

further characterised by its anilide (small thin leaflets from dilute alcohol) m.p. 126°. (Found : N, 7·9 per cent.; $C_{12}H_{12}ON$ requires N, 7·5 per cent.). *p*-toluidide of Δ^1-cyclopentanyl carboxylic acid crystallised in tiny needles from dilute alcohol, m.p. 122°. (Found : N, 7·4 per cent., $C_{13}H_{14}ON$ requires N, 7·2 per cent.) Ethyl Δ^1-cyclopentenyl carboxylate—prepared from the silver salt of the acid and ethyl iodide—was a colourless liquid b.p. 63° at 5 mm. (Nandi, *loc. cit.*, gives the b.p. as 71° at 11 mm.) It had $D_4^{24} = 0{\cdot}9971$ and $N_D^{24} = 1{\cdot}45906$, and iodine value = 2·61 (by Linstead and May's method).

Isolation of ethyl Δ^2-cyclopentenyl carboxylate.—The liquid left after separation of the acid (13 gms.), absolute alcohol (27 c.c.) and N-alcoholic HCl (12 c.c.) were mixed together and left at ordinary temperature for 5 hours. It was poured in dilute sodium carbonate solution, extracted with ether, washed, dried and the ester recovered. (Yield : 9 gms., b.p. 63–64° at 10 mm.) The alkaline solution gave 2 gms. of Δ^1-cyclopentenyl carboxylic acid on acidification. In the determination of the iodine number (Hanus) it was found that the ester gave different values for different intervals of time at ordinary temperature (25°). Hence 0–5° temperature and an interval of 3 hours were adopted as standard conditions for the determination of iodine number since consistent and repeatable results could only be obtained under these conditions. The iodine number (Hanus) of the above ester under the above conditions was 169, the theoretical value being 181·5. Hence it was again hydrolysed in cold and the acid recovered (6·5 gms.) re-esterified for 3 hours. Pure Ethyl Δ^2-cyclopentenyl carboxylate thus isolated (4 gms.) had b.p. 62° at 10 mm. $D_4^{29} = 0{\cdot}9797$, $N_4^{29} = 1{\cdot}44314$. Iodine number (Hanus) = 179·5 (theoretical 181·5). It had iodine value = 88·3 (according to Linstead and May's method). (Found : C, 68·3; H, 8·7 per cent.; $C_8H_{12}O_2$ requires C, 68·6; H, 8·6 per cent.)

Δ^2-cyclopentenyl carboxylic acid.—Thr above ester (3.5 gms.) on hydrolysis in cold gave cyclopentenyl carboxylic acid (2·5 gms.) b.p. 97–98° at 7 mm. It had $D_4^{26} = 0{\cdot}9867$, $N_D^{26} = 1{\cdot}46701$; Iodine number (Hanus) = 179·3 and iodine value = 22·7 (according to Linstead and May's method). (Found : C, 64·0; H, 7·3 per cent.; Eqt-Wt., 112·3; $C_6H_8O_2$ requires C, 64.3; H, 7·1 per cent.; Eqt-Wt., 112·0). the anilide of Δ^2-cyclopentenyl carboxylic acid crystallised from dilute alcohol in small thin rhombic plates m.p. 134–35°. (Found : N, 8·0 per cent.; $C_{12}H_{12}ON$ requires N, 7·5 per cent.) *p*-toluidide of Δ^2-cyclopentenyl carboxylic acid crystallised in pearly white shining plates, m.p. 126–27°. (Found: N, 7·3 per cent.; $C_{13}H_{14}ON$ requires N, 7·0 per cent.)

Summary

1. Δ^2-cyclopentenyl carboxylic acid is prepared for the first time and characterised by its various derivatives.

2. Corresponding Δ^1-acid and its derivatives are also described for comparison.

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RAMAN EFFECT IN ROCHELLE SALT CRYSTALS

By T. M. K. Nedungadi

(*From the Department of Physics, Indian Institute of Science, Bangalore*)

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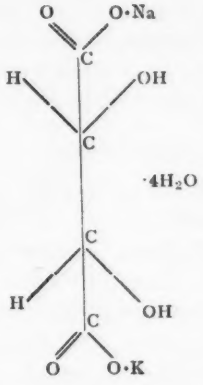
1. Introduction

It is well known that rochelle salt consists of potassium and sodium tartarate with four molecules of water of crystallisation. Its chemical constitutional formula is given as



The crystal belongs to the orthorhombic hemihedral class and has four molecules in the unit cell. Due to the large number of atoms contained in the unit cell and the consequent number of individual parameters to be determined, its structure has not fully yielded to X-ray analysis. However, in recent years the pronounced electrical properties of the crystal have been the subject of a large number of researches,[1] for, the dielectric properties of this material, particularly between the temperatures -18 and $+23{\cdot}7°$ C., appear to be as unique as the magnetic properties of iron. Nevertheless, all these experiments still leave open the question of the nature of the dipoles responsible for this remarkable property of rochelle salt. Indeed, studies on the scattering of light and the Raman effect in the substance under different experimental conditions may be expected to throw some light on the mechanism of its peculiar "ferro-electric" behaviour. In view of the fact that large clear crystals of rochelle salt are available or can be easily grown

from solution, it is surprising to note that no serious effort has been hitherto made in this direction. Indeed, a perusal of the previous literature shows that the only authors namely, Langer and Klein,[2] Nisi[3] as well as Canals and Peyrot[4] who studied the spectrum of the substance have recorded quite meagre data. However, subsequent investigation by Nayar[5] in this laboratory has shown that there are more lines in the spectrum than already have been observed; but even his observations appeared to be incomplete. Further, the crystal can be cut in the form of a rectangular parallelopiped with its edges respectively parallel to the crystallographic axes and it is to be expected that the characteristics of the spectrum should have remarkable changes depending upon the orientation of the crystal with respect to the directions of incidence and observation and also those of the vibrations of the incident light vector. In the above circumstances, a detailed study of the Raman effect in rochelle salt was called for and was undertaken by the present author. Though the investigations are not as yet completed, some striking observations have already been made and it appeared desirable to report the preliminary results in the present communication.

2. *Experimental*

The investigation was carried out at the room temperature (27° C.) with clear half crystals (measuring nearly 12 cms. × 6 cms. × 3 cms.) of rochelle salt grown by the Brush Development Company and marketed by the Central Scientific Company. The axes *a*, *b* and *c* were easily identified as the length of the half crystal lay along the *c*-axis and one of its plane faces was perpendicular to the *a*-axis. The crystal was cut into shape by means of a rubber band moistened with water, made to run over two pulleys by means of a motor and was polished on a moist ground glass plate. The polished faces were protected with a cover glass attached with a trace of canada balsam in xylene; otherwise the surface gradually became tarnished due to efflorescence. Though large crystals were employed, long exposures were found necessary to record intense spectra. In spite of the clearness of the crystal, imperfections existed in certain directions, probably, characteristic of the conditions and mode of growth of the specimen.

The spectrum of a saturated aqueous solution of rochelle salt was recorded in the usual manner. The solution was generally found to be strongly fluorescent; this trouble was, however, avoided in the present case as far as possible by using the salt purified by repeated crystallisation from solution. The state of polarisation of the Raman lines of the salt in solution was also studied. The entire investigation was carried out by means of a Hilger two-prism spectrograph.

3. Results

Three spectrograms obtained by the use of incident unpolarised light for different orientations of the crystal are reproduced in the Plate. Fig. 1c is particularly clear and intense and may be taken as giving the complete spectrum of rochelle salt. The detailed analysis of this spectrum is given in Table I. The frequency shifts (in wave numbers per centimeter) observed by the author in the crystal are listed in Table II along with those reported by the previous authors for comparison. In column 4 of the same Table are given the frequency shifts observed in rochelle salt solution along with their states of polarisation. The data available on the spectrum of sodium tartarate in solution as well as tartaric acid in the crystalline form are also included in this Table as they are useful in understanding the significance of the frequency shifts in rochelle salt crystal.

On the whole, 25 distinct frequency shifts in addition to four water bands have been recorded for the spectrum of the crystalline salt in the present investigation. A perusal of Table II at once shows that many new frequencies missed by the previous investigators have been recorded. It will be noticed that there is close correspondence between the frequency shifts observed in the crystal for shifts above 178 and those in the rochelle salt and sodium tartarate in solution. Besides the tabulated frequencies, a weak band in the neighbourhood of 1400 also appears to be present both in the crystal and in the solution superposed over the Raman lines in that region. All the lines in rochelle salt solution are observed to be polarised.

The structure of the water bands observed in the crystal is peculiar. The two main bands lie at 3262 and 3400. The latter is the stronger and has an intense maximum at 3400 while the former is a broad band extending over some 200 cms.$^{-1}$ without any marked intensity maximum. The two others 3468 and 3534 are much weaker and comparatively sharper. The existence of these two bands in the spectrum could be clearly seen in one of the spectrograms taken by Nayar using λ 4046 as the exciting radiation, λ 4358 being cut off from the incident radiation by means of a suitable filter.

An interesting observation made in the present investigation is that the Raman lines undergo remarkable changes in intensity for different orientations of the crystal *even when the incident light is unpolarised.* In Fig. 1c where the incident light is along the *a*-axis and the scattered light is along the *c*-axis, the lines 532, 990 and 2979 are very intense. However, in Fig. 1*b* when the direction of incidence is along *b* and that of observation is along *c* the above-mentioned lines are much weakened, while the lines like 847, 2935 and 1379 which are very weak in the former case are intense. The

characteristics of Fig. 1*a* when the incident light is along *a* and the scattered light is observed along *b*, are quite different from those of the other two. In this case the lines 532 and 990 are extremely weak while the line 1112 has

TABLE I

$p = \lambda\, 3650 \cdot 2$ $\quad i = \lambda\, 4077 \cdot 8$
$k = \lambda\, 4046 \cdot 5$ $\quad e = \lambda\, 4358 \cdot 3$

No.	Wave-number	Assignment	No.	Wave-number	Assignment
1	24668	k–38	26	22558	e–380
2	24618	k–88	27	22454	e–484
3	24575	k–131	28	22407	e–531
4	24455	p–2934	29	22327	e–611
5	24409	p–2980	30	22297	e–641
6	24220	k–486	31	22239	e–699
7	24173	k–533	32	22127	e–811
8	23895	k–811	33	22092	e–846
9	23858	k–848	34	22048	e–890
10	23814	k–892	35	22023	e–915
11	23792	k–914	36	21947	e–991
12	23717	k–989	37	21869	e–1070
13	23636	k–1070	38	21825	e–1113
14	23596	k–1110	39	21771	k–2935
15	23527	i–989	40	21727	k–2979
16	23496	k–1210	41	21647	e–1291
17	23413	k–1293	42	21592	e–1346
18	23358	k–1348	43	21569	e–1379
19	23327	k–1379	44	21513	e–1425
20	23280	k–1426		Water bands	
21	22899	e–39			
22	22850	e–88	45	21555–21362	k–3151–3344
23	22806	e–132	46	21306	k–3400
24	22760	e–178	47	21238	k–3468
25	22689	e–249	48	21172	k–3534

TABLE II

Frequency shifts in Rochelle salt			Rochelle salt solution (Author)	Sodium tartarate solution (Edsall)[6]	Tartaric acid crystals (Gupta)[7]
Canals and Peyrot	Nisi	Author			
		39			36 (2)
		88			80 (1)
		132			103 (1)
		178			124 (2)
		249		239 (½ b)	
	362 (m)	380	376 (1 b)	378 (1 b)	
	484 (vf)	485		491 (0)	
	531 (m)	532	530 (3 d) P	532 (2 b)	
	614 (vf)	611	612 (1 b) P	618 (1 b)	
		641			
		699	722 (0)	719 (½ b)	731 (3)
	806 (vf)	811	803 (6) P	805 (4)	
		847	841 (1 s)	844 (½)	840 (1)
	892 (f)	891	890 (6) P	893 (4)	895 (1 b)
		915			
	990 (m)	990	991 (10 s) P	992 (6)	
	1069 (vf)	1070	1061 (3 s) P	1068 (3 b)	
		1112	1117 (1 b) P	1121 (3 b)	1141 (½ b)
1213		1210	1227 (1 b)	1224 (2 b)	
1292		1292		1310 (2 b)	
1348	1351 (f)	1347	1357 (7 d) P	1370 (5 b)	
1391	1387 (f)	1379			
1435	1436 (f)	1425	1424 (8 d) P	1418 (6 b)	
1639				1617 (1 b)	1745 (1 b)
2940	2934 (m)	2935	2933 (6bd) P	2936 (8 vb)	2944 (½)
2987	2981 (st)	2979			2970 (2)
3244	3303 (m)	3262			
3417	3405 (m)	3400			
3472		3468			
		3534			

P—Polarised line, f—faint, m—medium, st—strong, d—diffuse, b—broad.

come up with great intensity. However, the full characteristics cannot be made out from Fig. 1*a* due to the imperfection of the spectrogram. The very low frequency lines do not undergo marked changes with orientation of the crystal. However, some changes such as the weakening of the line 178 in Fig. 1*b* and of 132 in Fig. 1*a* are fairly clear. The water bands appear to undergo variations in intensity with orientation of the crystal; but the magnitudes of these changes are not clear on account of the strong background in Figs. 1*a* and 1*b*. Further it is observed that interchanging the direction of the incident light and that of observation of the scattered light for any particular orientation of the crystal does not change the characteristics of the spectrum as is to be expected theoretically. The intensities of the various lines for the three orientations of the crystal studied are recorded in Table III.

TABLE III

Intensities of the lines				Intensities of the lines			
Line	Incident light along *a* observation along *c*	Incident light along *b* observation along *c*	Incident light along *a* observation along *b*	Line	Incident light along *a* observation along *c*	Incident light along *b* observation along *c*	Incident light along *a* observation along *b*
39	5	4?	..	891	5	7	8
88	6 (bd)	5 (bd)	..	915	1	0	..
132	8 (s)	8 (s)	..	990	15	6	3
178	10 (vb)	6 (vb)	..	1070	5	7	3
249	5 (d)	(3 d)	..	1112	1	3	12
380	3 (bd)	1 (bd)	?	1210	4	3	6
485	4 (d)	3 (d)	2 (d)	1292	4 (d)	4	..
532	13	3	1	1347	5 (d)	4 (d)	4
611	4 (d)	4 (d)	..	1389	1	7	..
641	3 (d)	0	..	1432	3(d)	4 (d)	..
699	1 (d)	1	..	2935	6	15	4
811	5 (d)	4 (d)	6 (d)	2979	15	8	15
847	2	5	2	3262	5 (vbd)		
				3400	10 (d)		
				3468	2 (d)		
				3534	2 d		

4. Discussion of Results

A comparative study of the data given in Table II reveals that the frequency shifts above 178 can be attributed to the tartarate ion. The two sharp lines at 2935 and at 2979 are obviously due to the C–H oscillation of the ion. In the solution, however, these two lines are diffuse and slightly shifted so that they merge out into one another to form a well-polarised broad band with an intensity maximum at about 2940. The group of lines in the neighbourhood of 900 (for example, lines 811, 891 and 990) are due to the C–C oscillations of the ion. These lines, particularly the two latter ones, do not shift from their positions even in the solution. The fundamental frequencies attributed to the C–OH grouping should lie in the region 1050–1090 and hence the line 1070 may possibly be due to this group. There is some uncertainty in interpreting the strong line 532 as there can be no valence oscillation of such a low frequency value. The spectrum of tartaric acid also contains this line with undiminished frequency and thus it is obvious that ionisation has no effect on this frequency. This line then should correspond to a deformation oscillation of the carbon chain in the ion. Similar assignment of some of the lines below 600 cm.$^{-1}$ observed in many of the carboxylic acids has been made by Edsall.

It is noteworthy that no line corresponding to the carbonyl frequency is observed in the 1700 region either in the crystal or in the solution. There is strong reason to believe that the line 1639 observed by Canals and Peyrot in crystalline rochelle salt is due to the deformation oscillation of the water of crystallisation and corresponds to the line 1617 observed by Edsall in sodium tartarate solution which is evidently due to the solvent. The absence of the $C=O$ frequency in the present investigation is in accord with the idea established by Gupta[8] as well as by Edsall,[6] that the ionised carboxyl group does not give rise to this frequency or even if it does, the corresponding line would be extremely weak. Due to resonance the ionised carboxyl group closely resembles a bent symmetrical triatomic molecule in the symmetrical structure $\left[R—C\begin{matrix}\nearrow O \\ \searrow O\end{matrix}\right]^-$. The symmetric valence oscillation of this group falls generally at 1400 and is polarised. The line 1379 in rochelle salt crystal corresponds to this oscillation. In the solution the same line shifts to a lower value 1357. The ionised carboxyl group should give, besides, an asymmetric valence vibration at about 1580 and a symmetric deformation oscillation at 600. The line 611 may correspond to the latter line. The former should be a very weak line and probably is not recorded in the spectra studied. Further, the fact that all the lines in the spectrum of

the solution are completely polarised indicates that the tartarate ion is completely unsymmetrical.

Lattice Oscillations.—The four lines at 39, 88, 132 and 178 are characteristic of the crystalline lattice of rochelle salt as they do not appear in the spectrum of the salt in solution. Out of these, the lines 39 and 132 are very sharp and the other two are rather diffuse. The diffuseness of the line 178 may be partly due to its superposition over a weak low frequency water band at 170 cm.$^{-1}$ It is interesting to note that tartaric acid in the crystalline state also yields four lattice lines. Lines 39 and 88 in rochelle salt correspond very well in frequency to the lines 36 and 80 in tartaric acid and hence the forces involved in the oscillations of the lattice which give rise to these lines in rochelle salt are forces of the Vander Waals type. On the other hand, the lines 132 and 178 do not agree with the lines 103 and 124 in tartaric acid and hence the forces brought into play in these oscillations are forces of the ionic type. Gupta has recently studied the spectra of tartaric acid and sodium tartarate in the crystalline form. While the four low frequency lines mentioned above have been observed by him in tartaric acid, he has not been able to record similar lines in sodium tartarate. This fact has been made use of by him to support his arguments that these low frequency lines are due to intermolecular oscillations of polymerised groups and not due to lattice vibrations of the crystal. As can be seen in Fig. 1c of the present paper, very intense low frequency lines have been recorded for the exactly analogous ionic crystal of rochelle salt.

Effect of Crystal Orientation.—The striking changes in the intensity of many of the Raman lines with orientation of the crystal have already been described. A careful comparison of the three spectra reproduced in the Plate shows that the lines 532, 641, 847, 990, 1112, 1379, 2935 and 2979 undergo marked changes in intensity whereas the lines 249, 485, 811, 891, 1210, 1292, 1346 and 1425 do not show any fluctuation of intensity for the three orientations of the crystal. The rest of the lines show correspondingly only very slight changes in intensity. This different behaviour of the Raman lines is to be expected in the case of orthorhombic crystals. Recently Saxena[9] has indicated that the Raman lines in crystals can be considered to be due to the deformations of the optical polarisibility ellipsoid of the solid produced by the internal vibrations and can be expressed in terms of the six components of the change of the polarisibility tensor. The selection rules for these oscillations give the particular tensor components that are responsible for them and on these depend the intensities of the corresponding lines. From symmetry considerations, all the vibrations in orthorhombic crystals can be classed as either symmetric or antisymmetric. It is seen

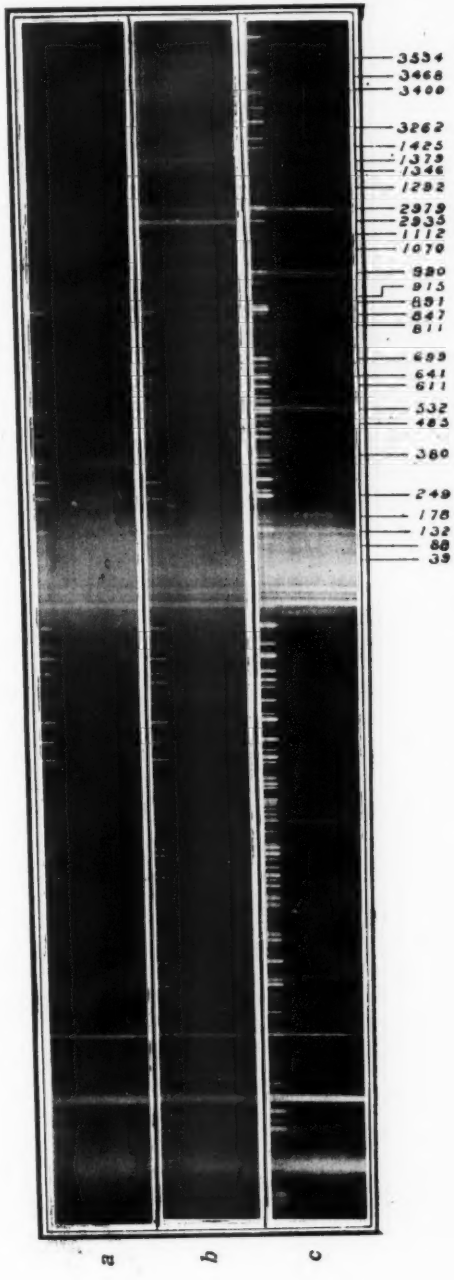


FIG. 1. Raman Spectrum of Rochelle Salt

a. Light incident along *a* axis and scattered along *b* axis
b. " " *b* " " " *c* "
c. " " *a* " " " *c* "

accordingly that the intensity of the symmetric oscillations should change markedly for the three orientations of such a crystal whereas the antisymmetric oscillations should not show similar changes. Thus the lines mentioned above which change in intensity markedly with orientation should be classed as symmetric oscillations while those which are fairly constant in intensity should be classed as antisymmetric oscillations. However, further study by the use of incident polarised light is necessary for clarification of the above classification of the lines. Work in this direction is in progress.

Finally, the author wishes to express his grateful thanks to Prof. Sir C. V. Raman for his keen interest and encouragement in the course of this work. The author's thanks are also due to Dr. C. S. Venkateswaran for useful discussion.

5. *Summary*

In a careful study of the Raman spectrum of a single crystal of rochelle salt, 25 distinct Raman shifts are recorded along with 4 water bands, many of them being reported for the first time. These shifts are compared with those observed by the author in a saturated solution of the salt in water. The most interesting effect observed in the study is that the intensities of many of the Raman lines change markedly for varying orientations of the crystal axes with respect to the directions of incidence and observation *even when the incident light is unpolarised.* Those lines which change in intensity conspicuously with orientation of the crystal are presumably to be classed as the symmetrical oscillations while those which do not show any change are similarly included under antisymmetric oscillations.

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THE ACTION OF HEXAMETHYLENETETRAMINE ON THE METHYL ESTERS OF PHENOLCARBOXYLIC ACIDS

Part I. The Synthesis of 2: 4-Dihydroxy-5-formyl-benzoic Acid

By R. D. Desai and (Miss) K. S. Radha

(From the Department of Chemistry, St. Xavier's College, Bombay)

Received March 20, 1940

A convenient method for the introduction of a formyl group (CHO) into salicylic acid was discovered by Duff and Bills[1], but when they tried to generalise it using monohydric phenols, the reaction was found to be abnormal and eccentric. However, Späth and Pailer[2] introduced the formyl group into 7-hydroxy-coumarin, whilst Rangaswamy and Sheshadri[3] prepared aldehydo-hydroxy-coumarins, -chromones, and -flavones by the same method. Our attempts to extend this method to the dihydric phenols failed but when the methyl ester of β-resorcylic acid was taken, an excellent yield of an aldehydo-acid was obtained. It gave readily the semicarbazone, the 4-nitrophenylhydrazone and 2 : 4-dinitrophenylhydrazone. On decarboxylation, it was converted into β-resorcylaldehyde, whilst its m.p. was considerably depressed by an admixture with an authentic specimen of the isomeric 2 : 4-dihydroxy-3-formyl benzoic acid which was kindly supplied by Dr. R. C. Shah of the Royal Institute of Science, Bombay. The acid had, therefore, the only possible constitution of 2 : 4-dihydroxy-5-formylbenzoic acid. Other interesting properties of this acid, as well as the extension of this reaction to the methyl esters of other hydroxy acids are being actively pursued.

Experimental

Preparation of 2 : 4-*dihydroxy-5-formylbenzoic acid.*—A mixture of anhydrous methyl β-resorcylate (10 g.), hexamethylene tetramine (30 g.) and glacial acetic acid (50 c.c.) was refluxed on sand-bath for 10 hours, and further 3–4 hours after the addition of dilute (1 : 1) hydrochloric acid (100 c.c.). The solid that separated out on cooling the mixture was filtered off, washed and purified through a 5 per cent. sodium bicarbonate solution. The pale-yellow acid crystallised from benzene in yellowish, lustrous needles, m.p. 185–86°. The acid was soluble in alkali with a yellow colour while its alcoholic solution gave an intense red colouration with alcoholic ferric chloride. It was fairly soluble in warm alcohol, acetic acid, acetone, etc., but insoluble in petrol. (Yield : 45 per cent.) The reaction failed if the methyl

ester was replaced by the acid and a yellow solid having a high m.p. and containing an appreciable amount of nitrogen was formed. (Found: C, 52·6; H, 3·6, $C_8H_6O_5$ requires C, 52·8, H, 3·3 per cent.)

When the acid was mixed with an equal amount of Shah and Laiwalla's 2 : 4-dihydroxy-3-formylbenzoic acid, the m.p. was depressed to 159–62°. On heating its solution in glacial acetic acid containing traces of hydrochloric acid, in a sealed tube at 180°, it was decomposed into β-resorcylaldehyde, identified by a mixed m.p. with an authentic specimen. The *semicarbazone*, prepared by the usual method, was an amorphous powder which did not melt upto 290°. (Found: N = 17·4; $C_9H_9O_5N_3$ requires N, 17·6 per cent.)

The 4-*nitrophenylhydrazone* was an orange powder unmelted upto 280°. (Found : N, 13·2, $C_{14}H_{11}O_6N_3$ requires N, 13·24 per cent.)

The 2,: 4-*dinitrophenylhydrazone* was also an orange-red microcrystalline solid melting above 280°. (Found : N, 15·2; $C_{14}H_{10}O_8N_4$ requires N, 15·5 per cent.)

We take this opportunity to thank Prof. R. N. Bhagwat, M.A., B.SC., the Director of the Laboratories and Rev. G. Palacios, S.J., PH.D., D.D., the Principal, for their kind interest, and provision of the facilities.

Summary

An excellent yield of 2 : 4-dihydroxy-5-formyl-benzoic acid is obtained by the action of hexamethylene-tetramine on methyl β-resorcylate.

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RAMAN EFFECT AND CHEMICAL CONSTITUTION

Influence of Constitutive and other Factors on the Double Bonds in Organic Compounds

Part IV. The Frequency of the Ethylenic Double Bond in Unsaturated Carbonyl Compounds

By G. V. L. N. Murty and T. R. Seshadri

(From the Department of Chemistry, Andhra University, Waltair)

Received April 9, 1940

In a recent communication[1] it has been shown by us that a phenyl group attached directly to the carbon of the C = O lowers its frequency and this was attributed to the existence of resonance. This view has further been strengthened by the results obtained by us in the investigation of the C = O frequencies of the esters of phenyl acetic acid.[2]

A similar effect of an ethylenic double bond on the carbonyl frequency has been noted by many workers. When these groups are in conjugation the C = O frequency is markedly lowered as will be clear from the typical examples given in Table I.

In this respect the phenyl ring and the ethylenic double bond behave alike and the same mechanism should hold good for both. The lowering of the carbonyl frequency by the ethylenic link is also then due to the existence of resonance as expressed below :

As a result of conjugation both the double bonds should be weakened simultaneously and hence the C = C frequency should undergo reduction at the same time as the C = O. It has sometimes been stated that under these circumstances there is a slight increase in the frequency of the ethylenic double bond.[3] When carefully examined and when comparisons are effected between closely related groups of compounds we find that there is no such discrepancy and that the ethylenic double bond exhibits invariably a lowered frequency. The ideal cases for comparison are isomeric esters such as ethyl cinnamate and cinnamyl acetate, ethyl acrylate[4] and allyl acetate.[5] They are pairs having the same molecular weight, the same number and kind of

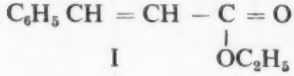
TABLE I

Formula of the Compound	C = O freq. in cm.$^{-1}$	Formula of the Compound	C = O freq. in cm.$^{-1}$	Formula of the Compound	C = O freq. in cm.$^{-1}$
$CH_3 \cdot CO \cdot CH_3$	1712	$CH_3 \cdot CHO$	1716	$CH_3 \cdot COOC_2H_5$	1739
$(CH_3)_2 \cdot C : CH \cdot CO \cdot CH_3$	1685	$CH_2 : CH \cdot CHO$	1692	$CH_2 : CH \cdot COOC_2H_5$	1718
$(CH_3)_2 \cdot C : CH \cdot CO \cdot CH : C \cdot (CH_3)_2$	1666	$CH_3 \cdot CH : CH \cdot CHO$	1685	$CH_3 \cdot CH : CH \cdot COOC_2H_5$	1713
$C_6H_5 \cdot CH : CH \cdot CO \cdot CH_3$	1666	$C_6H_5 \cdot CH : CH \cdot CHO$	1670	$C_6H_5 \cdot CH : CH \cdot COOC_2H_5$	1712
$C_6H_5 \cdot CH : CH \cdot CO \cdot C_6H_5$	1668	..	..	..	..

TABLE II

	C = C	C = O		C = C	C = O		C = C
Ethyl cinnamate ..	1634	1712	Cinnamyl acetate ..	1660	1673	Cinnamyl alcohol ..	1660
Ethyl acrylate ..	1635	1718	Allyl acetate ..	1649	1742	Allyl alcohol ..	1645
Ethyl crotonate (*trans*) ..	1653	1713	Crotonyl acetate (*trans*) ..	1679	1742	Crotonyl alcohol (*trans*) ..	1677
Ethyl isocrotonate (*cis*) ..	1644	1713	Isocrotonyl acetate (*cis*) ..	1664	1742	Isocrotonyl alcohol (*cis*) ..	1653

groups with the only difference that in one there exists conjugation between C = C and C = O groups and not in the other.



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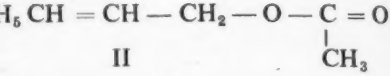

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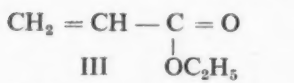
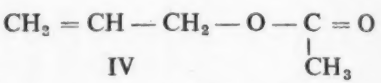


III



IV

Their spectra should be very similar in all respects except for the values of the C = C and C = O frequencies and they are found to be so. These frequencies are markedly lower for compounds I and III (Table II). It is remarkable that the ethylenic frequencies of II and IV are practically the same as those of cinnamyl and allyl alcohols from which the esters are derived, thus again showing that the electromeric effect arising from the carbonyl is the important factor responsible for lowering the ethylenic frequencies and that it is not transmitted when there is a CH_2 group in the way. Other examples derived from the crotonyl series are also given in Table II. It should be noted that in some cases the mutual lowering of the C = C and C = O frequencies is almost to the same extent.

The Raman spectra of cinnamyl acetate and cinnamyl alcohol were studies by Gredy[6] in 1936 but since they were obviously incomplete especially for effecting close comparison with related compounds they have now been reinvestigated. The liquids employed were pure samples from Kahlbaum which were subjected to repeated distillations under vacuum. The other experimental details are the same as those described in Part II of this series.

The results presented in Table III clearly indicate that cinnamyl alcohol and cinnamyl acetate excite many more lines than were observed by the previous investigator and that the spectra of cinnamyl alcohol and cinnamyl acetate bear a very satisfactory general agreement with those of the cinnamates studied already.

TABLE III

Cinnamyl acetate. (Murty and Seshadri.)	Cinnamyl acetate. (Gredy.)	Ethyl cinnamate. (Murty and Seshadri.)	Cinnamyl alcohol. (Murty and Seshadri)	Cinnamyl alcohol. (Gredy)
275 (1)	..	270 (1)	272 (0)	..
359 (1)	..	357 (1)	355 (1)	..
578 (1)	..	582 (1)	580 (1)	..
620 (2)	621	619 (2)	619 (2)	621
713 (2)	..	713 (2)	713 (2)	..
..	..	836 (1)	830 (0)	..
940 (2)	..	943 (2)	940 (1)	..
972 (2)	..	972 (2)	970 (1)	..
1000 (6)	1000	999 (7)	1000 (6)	1000
1030 (2)	1031	1030 (2)	1030 (1)	1031
1157 (1)	1158	1160 (2)	1160 (1)	1158
1180 (5)	..	1182 (5)	1180 (5)	..
1204 (6)	1208	1204 (6)	1202 (6)	..
1254 (1)	1281	1250 (2)	1250 (2)	1274
..	..	1305 (1)	..	..
1450 (1)	..	1450 (2)	1450 (1)	..
1512 (1)	..	1516 (1)	1516 (1)	..
1540 (2)	..	1540 (2)	1538 (1)	..
1578 (2)	..	1578 (2)	1576 (2)	..
1597 (2)	1600	1598 (7)	1598 (7)	1600
1660 (10)	*1659*	*1634* (10)	*1660* (10)	*1657*
1738 (5)	*1740*	*1712* (5*b*)	..	..
..	..	2940 (1)	..	..
3064 (1)	3062	3066 (1)	3066 (1)	3062

Summary

The Raman spectra of cinnamyl alcohol and cinnamyl acetate are re-investigated and their frequencies compared with those of ethyl cinnamate. A great similarity between the spectra of all these substances is observed. The higher C = C and C = O frequencies in cinnamyl acetate and allyl acetate as compared with ethyl cinnamate and ethyl acrylate is explained as due to the existence of resonance in the latter. It is pointed out that when comparisons are effected carefully the C = C and C = O bonds mutually weaken each other when they exist in conjugation.

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ON THE REPRESENTATION OF A NUMBER AS THE SUM OF THE kTH POWER OF A PRIME AND AN lTH POWER-FREE INTEGER

K. SAMBASIVA RAO

(From the Department of Mathematics, Andhra University, Waltair)

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Introduction

IN what follows all small letters stand for positive integers while p always denotes a prime and g_l an lth power-free integer, that is, an integer which is not divisible by the lth power of any integer except unity. Let

$$\psi(x) = a_0x^k + a_1x^{k-1} + \cdots + a_k$$

be an integral valued polynomial of the kth degree whose first coefficient is positive. $R_{k,l}(n)$ and $R'_{\psi,l}(n)$ denote the number of representations of n in the respective forms

$$n = p^k + g_l \tag{1}$$

and $$n = \psi(p) + g_l.$$

Estermann[1]* gave an asymptotic formula for $R_{1,2}(n)$ which was subsequently improved by A. Page[2] and still further by A. Walfisz[3]. Erdös[4] generalised Estermann's result by proving that $R_{2,2}(n) > 0$ for all sufficiently large $n \not\equiv 1 \pmod 4$. At the end of his paper Erdös mentioned that $R_{k,k}(n) > 0$. Pillai[5] recently gave an asymptotic formula for $R_{2,2}(n)$.

The purpose of the present paper is to evaluate $R_{k,l}(n)$ and $R'_{\psi,l}(n)$ for any k and all $l \geqslant k$ for the former and $l > k$ for the latter. Thus theorems 1 and 3 below constitute a generalisation of the results of the above writers. It may be noted that the value for $R_{2,2}(n)$ obtained from the theorem as a particular case with $k = 2$ and $l = 2$ is better than that obtained by Pillai, because of the improvement in the error-term.

In what follows LiX stands for

$$\int_2^x \frac{dx}{\log x}$$

* See the list of references at the end of the paper.

(m, t) denotes the g.c.d. of m and t. $\phi(m)$ and $\mu(m)$ are the well-known arithmetical functions. $T(m)$ denotes the number of distinct prime factors of m. $D(m, n) = D(m)$ denotes the number of solutions of the congruence

$$x^k \equiv n \pmod m$$

if $(m, n) = 1$, and zero otherwise. Similarly $D_\psi(m, n) = D'(m)$ denotes the number of solutions of the congruence

$$\psi(x) \equiv n \pmod m$$

with $(x, m) = 1$. Let

$$\gamma = \gamma(p, k) = \begin{cases} 2 \text{ if } p = 2,\ 2/k \\ 1 \text{ otherwise.} \end{cases}$$

$$P(l) = P(l, n) = \prod_p \left\{1 - \frac{(\gamma k, \phi(p^l))}{\phi(p^l)}\right\}$$

where p runs through all primes prime to n for which n is a kth power residue (mod p^l).

$$P'(l) = \prod_p \left\{1 - \frac{D'(p^l)}{\phi(p^l)}\right\}$$

where p runs through all primes. $\pi(X\ ;\ m, x)$ denotes the number of primes less than X which are of the form $mt + x$. h is any sufficiently large positive constant. ϵ is any arbitrarily small positive number. $c_1, c_2, \ldots$ are constants independent of n but dependent on one or more of ϵ, l, k, h and ψ.

THEOREM 1 : Let $l \geqslant k$. Then

$$R_{k,l}(n) = P(l)\, \mathrm{Li} n^{1/k} + O\left(\frac{n^{1/k}}{(\log n)^h}\right)$$

where the constant implied in O is independent of n.

Further

$$R_{k,l}(n) > C_1.\, \mathrm{Li}\, n^{1/k} \quad \text{for all sufficiently large}$$

(A) $$n \not\equiv 1 \begin{cases} \pmod{16} \text{ when } k = 4 \text{ and } l = 4 \\ \pmod{2^l} \text{ when } k = 2 \text{ and } l = 2 \text{ or } 3. \end{cases}$$

An interesting consequence of this theorem is

THEOREM 2 : Let $l > k$. Every sufficiently large n satisfying the conditions (A) is representable as the sum of the kth power of a prime and of an integer which is lth power-free but not $(l-1)$th power-free.

As a generalisation of Theorem 1 we have

THEOREM 3 : Let $l > k$. Then

$$R'_{\psi,l}(n) = P'(l)\ \ \mathrm{Li}\left(\frac{n}{a_0}\right)^{1/k} + O\left(\frac{n^{1/k}}{(\log n)^h}\right)$$

Further

$$R'_{\psi,k}(n) > C_2\ \mathrm{Li}\, n^{1/k} \qquad (2)$$

for all sufficiently large n if $\psi(x)$ is such that for any prime q there is no integer d such that

$$\psi(x) \equiv d \pmod{q^l} \text{ for all } (x, q) = 1.$$

Otherwise (2) holds for all sufficiently large

$$n \not\equiv d \pmod{q^l}$$

For the proof of theorem 1 we require the following lemmas :—

Lemma 1 : Given any positive constant h we can find another h_1 such that for

$$0 < m < (\log x)^{h_1} \text{ and } (m, x) = 1,$$

$$\pi(X ; m, x) = [\phi(m)]^{-1} \operatorname{Li} X + O(X [\phi(m) (\log X)^k]^{-1})$$

where the constant implied in the symbol is independent of X, m and x.

This is the well-known Siegel-Walfisz's[2] theorem. The theorem is quoted by Vinogradow in his book[6] in a form almost identical to the above.

Lemma 2 : The number of solutions in m, r, p of

$$m^l r + p^k = n \qquad \text{with } (m, n) > 1 \tag{3}$$

is $O(n^\epsilon)$.

Proof : From (3) it follows that $p \mid n$. Hence there are atmost $(\log n/\log 2)$ possibilities for p. Corresponding to any p there are $O(n^\epsilon)$ possibilities for m and r as factors of $(n - p^k)$. This proves the lemma.

Lemma 3 : Let $(p, n) = 1$. If the congruence

$$x^k \equiv n \pmod{p^l} \tag{4}$$

is solvable, then

$$D(p^l) = [\gamma k, \phi(p^l)]$$

Proof : (*i*) When $p > 2$, the lemma follows from the existence of a primitive root mod p^l.

(*ii*) For $p = 2$ and k odd, the lemma can be proved by induction. For, 1^k, 3^k leave distinct residues mod 4 and if 1^k, 3^k, . . . $(2^l - 1)^k$ leave distinct residues mod 2^l, then 1^k, 3^k . . . $(2^{l+1} - 1)^k$ also leave distinct residues mod 2^{l+1}.

(*iii*) Let $p = 2$ and $k = 2^r k_0$, where $r \geq 1$ and k_0 is odd. Then the lemma is evident for $l \leqslant r + 2$. It is true for $l = r + 3$ since

$$(4t \pm 1)^k \equiv \begin{cases} 1 \pmod{2^l} \text{ if } t \text{ is even,} \\ 1 + 2^{r+2} \pmod{2^l} \text{ if } t \text{ is odd.} \end{cases}$$

If the lemma is true for $l (= r + s, s \geqslant 3)$, then it is true for $l + 1$. We shall prove this by showing that when $D(2^l, n) > 0$,

$$D(2^l, n) = D(2^{l+1}, n) = D(2^{l+1}, n + 2^l). \tag{5}$$

Let x_1 be a solution of the congruence (4). Then the 2^r numbers

$$x_1 + t\,2^s, \quad t = 0, 1, \ldots 2^{r-1}$$

are all solutions of (4). But

$$x_1^k, (x_1 + 2^s)^k, , \ldots [x_1 + (2^r - 1)\,2^s]^k$$

are alternately congruent to n and $n + 2^l$ or $n + 2^l$ and $n \pmod{2^{l+1}}$. Also,

$$(x_1 + 2^l)^k, (x_1 + 2^s + 2^l)^k, \ldots$$

are congruent to the corresponding members of the above sequence with respect to modulus 2^{l+1}. Hence of the 2^{r+1} numbers considered 2^r numbers are congruent to n and the remaining to $n + 2^l \pmod{2^{l+1}}$. We can argue similarly for any other x_2, a solution of (4). Hence (5) and consequently the lemma are proved.

Lemma 4: Let $(q_1, q_2) = 1$. Then

$$D(q_1)\,D(q_2) = D(q_1\,q_2) \tag{6}$$

Proof: From the definition of $D(m)$ it is easily seen that when one of the sides of (5) vanishes the other also must vanish.

Further when $(q_1, q_2) = 1$, since $rq_2 + sq_1$ runs through the reduced residue system mod q_1, q_2 when r (consequently rq_2) and s (consequently sq_1) run through reduced residue systems mod q_1 and q_2 respectively, to any pair of solutions of

$$n \equiv (rq_2)^k \equiv (rq_2 + sq_1)^k \pmod{q_1}$$

and

$$n \equiv (sq_1)^k \equiv (rq_2 + sq_1)^k \pmod{q_2}$$

corresponds a solution of

$$n \equiv (rq_2 + sq_1)^k \pmod{q_1 q_2}$$

and the converse. Hence the lemma is proved.

Lemma 5: $\operatorname{Max} T(m) \sim \log m / \log \log m$.

Note.—An immediate corollary of this lemma is

$$\operatorname*{Lt}_{m \to \infty} \frac{T(m)}{\log m} = 0.$$

For indications of proof see Ramanujan's *Collected Papers*, page 263.

Lemma 6: $D(m) = O(m^\epsilon)$

Proof: When canonically represented let $m = p_1^{a_1} p_2^{a_2} \ldots p_r^{a_r}$. Then $r = T(m)$. By lemmas 4, 3 and 5 we have

$$D(m) = D(p_1^{a_1})\,D(p_2^{a_2}) \ldots D(p_r^{a_r}) > (2k)^{T(m)} = O(m^\epsilon).$$

Lemma 7: $\phi(m) > B \dfrac{m}{\log \log m}$,

where B is an absolute positive constant.

This is theorem 328 in *Introduction to Theory of Numbers* by Hardy and Wright.

Proof of Theorem 1 :

In what follows $\sum_{\substack{m,r,p \\ 1}}$ and $\sum_{\substack{m,r,p \\ 2}}$ denote summations extended over all m, r, p satisfying the relation $m^l r + p^k = n$ with $(m, n) = 1$ and $(m, n) > 1$ respectively.

Since $\sum_{\substack{m,r \\ m^l r = h}} \mu(m) = 1$ or 0 according as h is or is not lth power-free, we have,

$$\begin{aligned} R_{k,l}(n) &= \sum_{\substack{m,r,p \\ m^l r + p^k = n}} \mu(m) \\ &= \sum_{\substack{m,r,p \\ 1}} \mu(m) + \sum_{\substack{m,r,p \\ 2}} \mu(m) \\ &= \sum_{\substack{m,r,p \\ 1}} \mu(m) + O(n^\epsilon) \text{ by lemma 2.} \\ &= \sum_{\substack{m,r,p \\ 1 \\ m \leqslant n^{1/k-2\epsilon}}} \mu(m) + \sum_{\substack{m,r,p \\ 1 \\ m > n^{1/k-2\epsilon}}} \mu(m) + O(n^\epsilon) \qquad (10) \end{aligned}$$

But

$$\left| \sum_{\substack{m,r,p \\ 1 \\ m > n^{1/k-2\epsilon}}} \mu(m) \right| \leqslant \sum_{\substack{m,r,p \\ 1 \\ r < n^{2\epsilon}}} | = O\left(\sum_{r < n^{2\epsilon}} n^{1/k+1} \right)$$

$$= O\left(\frac{n^{1/k}}{(\log n)^h} \right) \qquad (11)$$

since the number of solutions of

$$ax^l + by^k = n$$

is $O(n^{1/k+1})$ for $l > k$ by trivial considerations and is $O[d(n)]$ for $l = k$ by a result of Oppenheim.[7]

Put

$$\begin{aligned} Q_1 &= \sum_{\substack{m,r,p \\ 1 \\ m \leqslant n^{1/k-2\epsilon}}} \mu(m) \\ &= \sum_{m \leqslant n^{1/k-2\epsilon}} \mu(m) \sum_{x_s} \pi(n^{1/k}; m^l, x_s) \\ &= \sum_{m < (\log n)^{h_1}} \mu(m) \sum_{x_s} \pi(u^{1/k}; m^l, x_s) \\ &\quad + \sum_{(\log n)^{h_1} \leqslant m \leqslant n^{1/k-2}} \mu(m) \sum_{x_s} (\pi n^{1/k}; m^l, x_s) \\ &= Q_1' + Q_1'', \text{ say,} \qquad (12) \end{aligned}$$

where $x_1, x_2, \ldots x_D$ are the distinct roots of the congruence

$$x^k \equiv n \pmod{m^l}, \ (m, n) = 1.$$

But it is easily seen that

$$|\, Q_1'' \,| = O\{ \sum_{(\log n)^{h_1} \leqslant m \leqslant n^{1/k - 2\epsilon}} ([n^{1/k}/m^l] + 2)\, m^\epsilon \}$$

$$= O\left(\frac{n^{1/k}}{(\log n)^h}\right) \tag{13}$$

I now put

$$Q_2 = \text{Li}\, n^{1/k} \sum_{\substack{m \\ (m, n) = 1}} \frac{\mu(m)\, D(m^l)}{\phi(m^l)} \tag{14}$$

Now by lemmas 1, 6 and 7 we have

$$|\, Q_1' - Q_2 \,| < \sum_{m < (\log n)^{h_1}} \sum_{x_s} \left| \pi(n^{1/k}; m^l, x_s) - \frac{1}{\phi(m^l)} \text{Li}\, n^{1/k} \right|$$

$$+ \text{Li}\, n^{1/k} \sum_{m \geqslant (\log n)^{h_1}} \frac{D(m^l)}{\phi(m^l)}$$

$$= O\left(\frac{n^{1/k}}{(\log n)^h}\right) \tag{15}$$

Hence from (10), (11), (12), (13), (14) and (15) we have

$$R_{k,l}(n) = Q_2 + O\left(\frac{n^{1/k}}{(\log n)^h}\right) \tag{16}$$

But by lemma 3,

$$\sum_{\substack{m \\ (m, n) = 1}} \frac{\mu(m)\, D(m^l)}{\phi(m^l)} = \prod_p \left(1 - \frac{D(p^l)}{\phi(p^l)}\right) \text{ extended over all } p$$

$$= \prod_p \left\{1 - \frac{[\gamma k, \phi(p^l)]}{\phi(p^l)}\right\} \tag{17}$$

$$= P(l),$$

where p runs through all primes for which the congruence

$$x^k \equiv n \pmod{p^l}, \ (p, n) = 1$$

is solvable.

Hence the first part of the theorem follows from (14), (16) and (17). To prove the second part we note that when n satisfies the condition (A) none of the factors of $P(l)$ vanishes and for $l \geqslant 2$, each factor is greater than $\frac{1}{2}$ when $p \leqslant k$ and greater than $1 - k/\phi(p^l)$ when $p > k$.

Hence

$$P(l) > (\tfrac{1}{2})^{\pi(k)} \cdot \prod_{p>k}\left(1-\frac{2k}{p^l}\right) = C_1 > 0$$

since the product $\prod_{p>k}\left(1-\frac{2k}{p^l}\right)$ is absolutely convergent.

Proof of Theorem 2: The theorem follows from the following lemmas.

Lemma 8 : Let n be any sufficiently large integer. There is always a prime between $C_4 \log n (\log\log n)^2$ and $2\,C_4 \log n (\log\log n)^2$ which belongs to a given arithmetic progression and which is prime to n.

Proof : Let k be the common difference. Then the number of primes in the given A. P. between the limits is

$$\pi(2\,C_4 \log n (\log\log n)^2 ; k, l) - \pi(C_4 \log n (\log\log n)^2 ; k, l)$$

$$\text{is} \sim \frac{C_4}{\phi(k)} \log n \,.\, \log\log n$$

But $T(n)$, the number of distinct prime factors of n is $O(\log n)$. Hence the lemma follows easily.

Lemma 9 :

$$\frac{P(l)}{P(l+1)} < 1 - \frac{1}{(\log n)^{2l}}.$$

Proof : It is easily seen that for $(p, k) = 1$

$$D(p^l) - D(p^{l+1})$$

and for $(p, k) > 1$

$$D(p^l) \geqslant D(p^{l+1})/p.$$

Hence for all p

$$1 - \frac{D(p^l)}{\phi(p^l)} \leqslant 1 - \frac{D(p^{l+1})}{\phi(p^{l+1})}.$$

If $p > k$ and $p \not\equiv 1 \pmod{k}$ then every integer n for which $(n, p) = 1$ is a kth power residue mod p^l. Hence if p is such a prime lying between the limits specified in lemma 8, we have

$$\frac{P(l)}{P(l+1)} < \left\{1-\frac{D(p^l)}{\phi(p^l)}\right\} \Big/ \left\{1-\frac{D(p^{l+1})}{\phi(p^{l+1})}\right\} = 1 - \frac{1}{\phi(p^l)} + O\left(\frac{1}{\phi(p^{l+1})}\right)$$

$$< 1 - \frac{1}{(\log n)^{2l}}$$

Hence if h is chosen to be sufficiently large, then

$$\{P(l+1) - P(l)\}\, \mathrm{Li}\, n^{1/k} > C_5 \frac{n^{1/k}}{(\log n)^k}.$$

Hence

$$R_{k,\,l+1}(n) - R_{k,l}(n) > 0.$$

This proves Theorem 2.

Proof of Theorem 3 : This is just similar to the proof of theorem 1. The necessary lemmas can be constructed and proved on analogous lines. But lemma 3 is to be replaced by

Lemma 10 : If $\psi(x)$ is a polynomial of degree k with non-zero discriminant Δ, then the congruence

$$\psi(x) \equiv 0 \pmod{p^l}$$

has not more than $k(\Delta^2, p^l)$ solutions.

This is due to Hua.[8]

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ON WARINGS' PROBLEM FOR BIQUADRATES

By F. C. Auluck
(*Dyal Singh College, Lahore*)

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1. There is much uncertainty about the value of $g(4)$. The best known results give the wide range $19 \leqslant g(4) \leqslant 35$.* The evaluation of $g(k)$ due to Pillai† and Dickson‡ depends upon the previous determination of $G(k)$ and the lower limit N_0 of numbers which can be expressed as the sum of $G(k)$ kth powers, followed by a "method of ascent". In the present paper we shall prove that, in the case of biquadrates, this lower limit is as large as $10^{10^{89}}$ which makes it practically unpossible to apply the above method to evaluate $g(4)$. If we assume the unproved result that a number cannot be represented as the sum of two biquadrates in more than two ways, N_0 comes out to be about $10^{10^{69}}$.

We shall use the Hardy-Littlewood method as modified by Gelbeke. References to Gelbeke are to his paper "Zum Waringschen Problem", *Mathematiche Annalen*, 105, 1931, p. 637–52, and will be denoted by G.

2. *Notation*

$r(n)$ denotes the number of solutions of $n = \sum_{\substack{1 \leqslant i \leqslant 15 \\ h_i \geqslant 0}} h_i^4$

$$\rho = \exp\left(2i\pi \frac{l}{q}\right) \qquad \text{where } (l, q) = 1$$

$$S_\rho = \sum_{z=1}^{q} \rho^{z^4}$$

$A(q, j) = \frac{1}{q^{15}} \sum_{\rho} S_\rho^{15} \rho^{-j}$ where ρ goes through all qth primitive roots of unity.

$$S(j, \lambda) = \sum_{q=1}^{\lambda} A(q, j)$$

$$f(x) = \sum_{h=0}^{n^{\frac{1}{4}}} x^{h^4}$$

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* The upper bound was found by Dickson, *Bull. American Math. Soc.*, 1933, **39**, 701–27. Pillai has recently proved that $g(4) \leqslant 27$ (*Math. St.*, 1939, VII, 144).

† *Jour. Ind. Math. Soc.*, 1936, **2**, (2), 16–44; *Proc. Ind. Acad. Sci.*, (A), 1936, **4**, 261.

‡ *American Jour. of Math.*, 1936, **58**, 521–29, 530–35.

$$\psi_\rho(x) = \Gamma(\tfrac{5}{4})\frac{S_\rho}{q}\left[1+\sum_{j=1}^{n}\frac{1\cdot5\cdot9\cdots(4j-3)}{4^j\,\underline{|j}}\left(\frac{x}{\rho}\right)^j\right]$$

$$\phi_\rho(x) = \Gamma(\tfrac{5}{4})\frac{S_\rho}{q}\sum_{j=n+1}^{\infty}\frac{1\cdot5\cdot9\cdots(4j-3)}{4^j\,\underline{|j}}\left(\frac{x}{\rho}\right)^j$$

$$\Psi_\rho(x) = \psi_\rho(x) + \phi_\rho(x) = \Gamma(\tfrac{5}{4})\frac{S_\rho}{q}\left(1-\frac{x}{\rho}\right)^{-\frac{1}{4}}$$

n denotes an integer greater than $n_0 = 10^{10^{10}}$. It can be easily verified that even without this restriction, the results cannot be improved.

3. *Farey Dissection*

On the circle $|x| = 1$ mark off the points $\rho = e^{2i\pi\frac{l}{q}}$ which correspond to the Farey fractions with denominators $\leqslant n^{\frac{1}{4}}$ and divide the circle into arcs by the mediants between neighbouring fractions. It is known that the arc which contains the point ρ stretches on either side of this point by something not more than $\frac{2\pi}{qn^{\frac{3}{4}}}$ and not less than $\frac{\pi}{qn^{\frac{3}{4}}}$. The arcs which correspond to $n^{\frac{1}{4}} < q \leqslant n^{\frac{1}{2}}$ are called m-arcs and those which correspond to $1 \leqslant q \leqslant n_{\frac{1}{4}}$ are called M-arcs. The M-arcs are subdivided in the following manner. The part of the M-arc which does not stretch more than $\frac{\pi}{q^{\frac{1}{2}\delta}n^{\frac{3}{4}\frac{1}{\delta}}}$ on each side of ρ will be denoted by M_1, the rest of the M-arc is called M_2-arc.

4. *Some General Lemmas*

Lemma 1. Let $|y| \leqslant \frac{1}{2}$, $a_0 \geqslant a_1 \cdots \geqslant a_N \geqslant 0$

$$\left|\sum_{j=0}^{N} a_j\, e^{2i\pi yj}\right| \leqslant \frac{a_0}{\sin\pi|y|}$$

Proof. Landau* Satz 140

Lemma 2. $$\int_{-\frac{1}{2}}^{\frac{1}{2}}\left|\sum_{j=0}^{N} a_j\, e^{2i\pi yj}\right|^2 dy = \sum_{j=0}^{N}|a_j|^2$$

Proof. Landau Satz 223

Lemma 3. Let $T(m)$ denote the number of divisors of m and ϵ any positive number, then

$$T(m) < C\, m^{\epsilon}$$

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* References to Landau are to his *Vorlesungen uber Zahlentheorie* (Leipzig, 1927), Volume I.

where $\mathsf{C} = \left(\frac{2}{e\,\epsilon \log 2}\right)^{\Pi\left(2^{\frac{1}{\epsilon}}\right)}$, $\pi(x)$ denotes the number of primes not exceeding x.

Proof. $m = \prod_{p|m} p^l$

$$\mathrm{T}(m) = \prod_{p|m} (l+1)$$

hence $$\frac{\mathrm{T}(m)}{m^\epsilon} = \prod_{p|m} \frac{l+1}{p^{l\epsilon}} \leqslant \prod_{p|m} \frac{l+1}{p^{l\epsilon}}$$

$$p < 2^{\frac{1}{\epsilon}}$$

(if $p \geqslant 2^{\frac{1}{\epsilon}}$, $p^{l\epsilon} \geqslant 2^l \geqslant 1 + l$)

Now $\frac{l+1}{p^{l\epsilon}}$ is maximum when $(l+1)\,\epsilon \log p = 1$

Hence $\frac{l+1}{p^{l\epsilon}} \leqslant \frac{p^\epsilon}{e\epsilon \log p} < \frac{2}{e\epsilon \log p}$ when $p^\epsilon < 2$

Therefore $$\frac{\mathrm{T}(m)}{m^\epsilon} \leqslant \prod_{p|m} \frac{2}{e\epsilon \log p}$$

$$p < 2^{\frac{1}{\epsilon}}$$

$$\leqslant \prod_{p < 2^{\frac{1}{\epsilon}}} \frac{2}{e\epsilon \log p}$$

$$\leqslant \left(\frac{2}{e\epsilon \log p}\right)^{\pi\left(2^{\frac{1}{\epsilon}}\right)}$$

Lemma 4. If $\mathrm{R}(m)$ is the number of solutions of $h_1^4 + h_2^4 = m$, $h_1, h_2 \geqslant 0$

$$\sum_{v=0}^{m} \mathrm{R}^2(v) \leqslant 16\,\mathsf{C} m^{\frac{1}{2}+\epsilon}$$

Proof. As $\mathrm{R}(m) \leqslant 4\,\mathrm{T}(m)$ and $\sum_{v=0}^{m} \mathrm{R}(v) \leqslant 4\,m^{\frac{1}{4}}$

therefore $$\sum_{v=0}^{m} \mathrm{R}^2(v) \leqslant \mathrm{Max}\ \mathrm{R}(v) \sum_{v=0}^{m} \mathrm{R}(v) \leqslant 16\,\mathsf{C} m^{\frac{1}{2}+\epsilon}$$

Lemma 5. If $\mathrm{S} = \sum_{h=1}^{m} e^{2\pi\lambda h^4 i}$ and $\lambda = \frac{l}{q}$

$$| S |^8 < 4^8 \left\{ m^7 + C^3 \, m^{4+9\epsilon} \left(\frac{24\, m^3}{q} + 1 \right) \left(m + \frac{2q^{1+\epsilon_1}}{\epsilon_1} \right) \right\}$$

where ϵ_1 is a positive number < 1.

Proof. This lemma follows from Landau Satzs 265–67 and lemma 3.

An inequality for Sρ.

Lemma 6†. $| S_\rho | \leqslant 20 \cdot 97 \, q^{\frac{1}{2}}$.

Proof. By Landau Satz 17, if ρ is a primitive pth root of unity.

$$| S_\rho | \leqslant 3\sqrt{p} \quad \text{if} \quad p \equiv 1 \pmod 4$$

and $$\leqslant \sqrt{p} \quad \text{if} \quad p \equiv -1 \pmod 4$$

Let $T_\rho = q^{-\frac{1}{2}} S_\rho$ where $q = p^l$

By Landau Satz 23, $T_\rho q = T_{\rho^{p^k}}$ for $l > 4^4$

It can be easily verified that when $p = 2$, $l \leqslant 4$

$$|S_\rho| = 2^l \operatorname{Cos} \frac{\pi}{2^l}$$

and so $| T_\rho | < 2$.

If p is odd

$$| T_\rho{}^{p^k} | = p^{-\frac{1}{2}} \, | S_\rho | \leqslant \begin{cases} 3p^{-\frac{1}{2}} & \text{if } p \equiv 1 \pmod 4 \\ p^{-\frac{1}{2}} & \text{if } p \equiv -1 \pmod 4 \end{cases}$$

and $$\left| T_{\rho^{p^l}} \right| = p^{-\frac{3l}{4}} \, p^{l-1} = p^{\frac{l}{4}-1} < 1 \quad \text{when } 2 \leqslant l \leqslant 4.$$

As $3p^{-\frac{1}{2}} \leqslant 1$ if $p \geqslant 81$, we need consider primes $\leqslant 79$.

Hence $$| T_{\rho^q} | = \prod_{p/q} \left| T_{\rho^{p^l (q,\, p)}} \right|$$

$$\leqslant 2, \prod_{\substack{p \leqslant 79 \\ p \equiv 1 \pmod 4}} (3p^{-\frac{1}{2}})$$

and the lemma follows.

The Singular Series

Lemma 7. If $S_\rho = \sum_{m=1}^{q} \rho^{m^4}$

and $$A_q = \sum_\rho \left(\frac{S_\rho}{q} \right)^{15} \rho^{-n}, \quad 16 \times n$$

† References to Landau, in this lemma, are to *Uber Einige Neuere Fortschritte der Additiven Zahlentheorie*, Cambrigde Tracts in Mathematics and Mathematical Physics, No. 35.

ρ going through all the $\phi(q)$ primitive qth roots of unity

and $$S(n) = \sum_{q=1}^{\infty} A_q$$

then $$S(n) > \frac{1}{10^{63 \cdot 57}}.$$

Proof. By Landau Satz 302

$$\chi_p = \sum_{l=0}^{\infty} A_{p^l} \geqslant w^{-14}$$

where $w = p^b$ and $b = \begin{cases} 4 & \text{if } p = 2, 16 \times n \\ 1 & \text{if } p > 2 \end{cases}$

Also Landau Satz 311, 293, 307 and 321

give $$\chi_p > 1 - \frac{3^{15}+1}{p^{\frac{13}{2}}} > 0 \quad \text{if } p \geqslant 13$$

therefore $$S > \frac{1}{16^{14}} \frac{1}{(3 \cdot 5 \cdot 7 \cdot 11)^{14}} \prod_{p \geqslant 13} \left(1 - \frac{3^{15}+1}{p^{\frac{13}{2}}}\right)$$

Since $$\log(1-u) > -\frac{u}{1-u} \quad \text{if } 0 < u < 1$$

$$\log \prod_{p \geqslant \xi} \left(1 - \frac{k}{p^r}\right) > -k \sum_{p \geqslant \xi} \frac{1}{p^r - k} > -\frac{k}{\xi^r - k} - k \int_{\xi}^{\infty} \frac{dx}{x^r - k}$$

But $$k \int_{\xi}^{\infty} \frac{dx}{x^r - k} = \xi \left\{ \frac{1}{r-1} \frac{k}{\xi^r} + \frac{1}{2r-1} \frac{k^2}{\xi^{2r}} + \cdots \right\}$$

$$< \frac{\xi}{r-1} \left\{ \frac{k}{\xi^r} + \frac{1}{2} \frac{k^2}{\xi^{2r}} + \cdots \right\} = -\frac{\xi}{r-1} \log \left(1 - \frac{k}{\xi^r}\right)$$

hence $\prod_{p \geqslant 13} \left(1 - \frac{3^{15}+1}{p^{\frac{13}{2}}}\right) > \frac{1}{10^{3 \cdot 828}}$ and the lemma follows.

Lemma 8.

$$\gamma'(\beta) \frac{j^\beta}{j+1} < \left| \frac{\Gamma(1+\beta+j}{j!} - j^\beta \right| < \gamma(\beta)\, j^{\beta-1}$$

where $$\gamma(\beta) = \begin{cases} \Gamma(2+\beta) & \text{if } \beta \leqslant 1 \\ \frac{\beta(\beta+1)}{2} \Gamma(2+\beta) & \text{if } \beta \geqslant 1 \end{cases}$$

and $$\gamma'(\beta) = \begin{cases} 1 & \text{if } \beta \geqslant 1 \\ \frac{\beta(\beta+1)}{2} & \text{if } \beta \leqslant 1 \end{cases}$$

Proof. Let $\dfrac{\Gamma(1+\beta+j)}{j!\, j^{\beta}} = \phi(j)$

$$\phi(j-1) - \phi(j) = \phi(j-1)\left\{1 - \frac{\beta+j}{j}\left(1-\frac{1}{j}\right)^{\beta}\right\}$$

It can be verified that for $j > 1$

$$y = j^2\left\{1 - \frac{\beta+j}{j}\left(1-\frac{1}{j}\right)^{\beta}\right\}$$

is an increasing function of j if $\beta > 1$
and is a decreasing function of j if $\beta < 1$.

Also $\qquad \dfrac{\beta(\beta+1)}{2} \leqslant y \leqslant 1 \quad$ if $\beta \leqslant 1$

and $\qquad 1 \leqslant y \leqslant \dfrac{\beta(\beta+1)}{2} \quad$ if $\beta \geqslant 1$

Defining $\qquad z_j = \dfrac{\phi(j)}{\Gamma(2+\beta)}$ we notice that $\dfrac{z_j}{z_{j-1}} < 1$

for $\beta > 0$ and therefore z_j is a decreasing function of j

Hence $\qquad 1 < \phi(j) \leqslant \Gamma(2+\beta) \quad$ for $j \geqslant 1$.

and $\dfrac{\beta(\beta+1)}{2}\dfrac{1}{j^2} < \phi(j-1) - \phi(j) \leqslant \Gamma(2+\beta)\dfrac{1}{j^2}$ If $\beta \leqslant 1$

$$\frac{1}{j^2} < \phi(j-1) - \phi(j) < \frac{\beta(\beta+1)}{2}\Gamma(2+\beta)\frac{1}{j^2} \quad \text{if } \beta \geqslant 1$$

Again $\qquad \left|\dfrac{\Gamma(1+\beta+j)}{j!\, j^{\beta}} - 1\right| - |\phi(j) - 1|$

$$= \sum_{v=j+1}^{\infty} |\phi(v-1) - \phi(v)| \qquad \{\operatorname*{Lt}_{j\to\infty} \phi(j) = 1$$

Noticing that $\qquad \dfrac{1}{j} > \sum_{v=j+1}^{\infty}\dfrac{1}{v^2} > \dfrac{1}{j+1}$

we get the result.

5. *Lemmas for the Whole Circle*

Lemma 9. On the circle $|x| = 1$

$$|\psi_\rho(x)| < 21{\cdot}0\, n^{\frac{1}{2}}\, q^{-\frac{1}{2}}$$

Proof. Lemmas 6 and 8.

Lemma 10. If $\dfrac{x}{\rho} = e^{2i\pi y}$ and $|y| \leqslant \frac{1}{2}$ then

$$|\phi_\rho(x)| < 2{\cdot}65\, n^{-\frac{1}{2}} q^{\frac{1}{2}} |y|^{-1}$$

and $\qquad |\Psi_\rho(x)| < 16{\cdot}0\, q^{-\frac{1}{2}} |y|^{-\frac{1}{2}}$

Proof. Lemmas 6 and 8.

Lemma 11. $\qquad |\psi_\rho(x)| < 21{\cdot}0\, q^{-\frac{1}{2}}$ Min $(n^{\frac{1}{2}}, |y|^{-\frac{1}{2}})$

Proof. Lemmas 9 and 10.

Lemma 12. $\sum_{M_1} \int_{R-M_1} |\psi_\rho^{15}(x)|^2 \, |dx| < 10^{42\cdot2} n^{\frac{41}{8}}$

the integration stretches to the whole circle R except the arc M_1, the summation being carried over all M_1-arcs.

Proof. If $q < n^{\frac{1}{8}}$, $\frac{1}{2n} < \frac{1}{2q^{\frac{9}{10}} n^{\frac{31}{40}}} < \frac{1}{2q^{\frac{3}{4}}}$

and $\int_{R-M_1} |\psi_\rho^{15}(x)|^2 \, |dx| < (21\cdot0)^{30} 2\pi q^{-\frac{15}{2}} \int_{\frac{1}{2q^{\frac{9}{10}} n^{\frac{31}{40}}}}^{\infty} y^{\frac{15}{2}} dy$ *

$< 10^{41\cdot7} n^{\frac{403}{800}} q^{-\frac{33}{20}}$

The number of arcs with *one* and the same q does not exceed q, hence

$$\sum_{M_1} \int_{R-M_1} |\psi_\rho^{15}(x)|^2 \, |dx| < 10^{41\cdot7} n^{\frac{403}{800}} \sum_{q=1}^{n^{\frac{1}{8}}} q^{-\frac{13}{20}}$$

$$< 10^{42\cdot2} n^{\frac{41}{8}}$$

6. *Lemmas for the* m-*Arcs*

Lemma 13. On m, $|f(x)| < \frac{50C^{\frac{3}{8}}}{\epsilon_1^{\frac{1}{8}}} n^{\frac{7+9\epsilon+3\epsilon_1}{32}}$.

Proof. By Gelbeke Satz 10 and lemma 5.

Lemma 14. $\sum_m \int_m |f^{15}(x)|^2 \, |dx| < \frac{10^{45\cdot68}}{\epsilon_1^{\frac{13}{4}}} n^{\frac{99+133\epsilon+39\epsilon_1}{16}}$

Proof. L.H.S. $<$ Max $|f(x)|^{20} 2\pi \int_{-\frac{1}{2}}^{\frac{1}{2}} |f^2(e^{2i\pi y})|^2 \, dy$

$f^2(x) = \sum_{j=0}^{2n} R(j) x^j$, $\begin{cases} R(j) = r_{4,2}(j) & \text{if } 0 \leqslant j \leqslant n \\ \text{and } 0 \leqslant R(j) \leqslant r_{4,2}(j) & \text{if } n < j \leqslant 2n \end{cases}$

$r_{4,2}(m)$ is the number of ways in which m can be represented as the sum of two biquadrates.

By lemmas 2, 4

$$\int_{-\frac{1}{2}}^{\frac{1}{2}} |f^2(e^{2i\pi y})|^2 \, dy = \sum_{j=0}^{2n} R^2(j) < 16\, C\, (2n)^{\frac{1}{2}+\epsilon}$$

and the lemma follows.

7. *Lemmas for the* M_1*-arcs*

Lemma 15. If $\frac{x}{\rho} = e^{2i\pi y}$, $|y| \leqslant \frac{1}{2}$ then

$$|f(x) - \psi_\rho(x)| < \frac{51 \cdot 9}{\epsilon_1^{\frac{1}{8}}} C^{\frac{3}{8}} q^{\frac{7}{8}+\frac{9\epsilon+\epsilon_1}{8}} \operatorname{Max}(n|y|, 1)$$

Proof. By using Gelbeke Satz 12 and lemmas 5 and 8, and noticing that $C \gg 10^5$ we get the result

Lemma 16.

$$\sum_{M_1} \int_{M_1} |f^{15}(x) - \psi_\rho^{15}(x)|^2 |dx| < \frac{10^{60.4} C^{\frac{45}{4}}}{\epsilon_1^{\frac{15}{4}}} n^{\frac{97+135\epsilon+15\epsilon_1}{16}}$$

Proof. Put $f(x) - \psi_\rho(x) = \Phi_\rho(x)$

$$|f^{15}(x) - \psi_\rho^{15}(x)|^2 < 2^{30}\{|\Phi_\rho^{30}(x)| + |\Phi_\rho^2(x)| \, |\psi_\rho^{28}(x)|\}$$

Evaluate $\int_{M_1} |f^{15}(x) - \psi_\rho^{15}(x)|^2 \, |dx|$ by the help of lemmas 15 and 11, splitting the range of y into two intervals $\left(0, \frac{1}{n}\right)$ and $\left(\frac{1}{n}, \frac{1}{q^{\frac{9}{10}} n^{\frac{31}{40}}}\right)$. Now multiply by q and integrate again with respect to q from 0 to $n^{\frac{1}{4}}$.

8. *Lemmas for the* M_2*-arcs*

Lemma 17. Let $\frac{x}{\rho} = e^{2i\pi y}$, $|y| \leqslant \frac{1}{2}$ then on an M_2-arc

$$|f(x)| < \frac{7 \cdot 84}{\epsilon_1^{\frac{1}{4}}} C^{\frac{3}{8}} n^{\frac{1}{8}+\frac{9\epsilon}{32}} q^{-\frac{1+\epsilon_1}{8}} |y|^{-\frac{1+\epsilon_1}{8}}$$

Proof. On an M_2-arc $1 < q < n^{\frac{1}{4}}$

$$x = e^{2i\pi\left(\frac{l}{q}+y\right)}, \quad \frac{1}{2q^{\frac{9}{10}} n^{\frac{31}{40}}} \leqslant |y| < \frac{1}{qn^{\frac{31}{4}}}.$$

By Gelbeke Satz 14, there exist numbers l_1, q_1, y_1 satisfying the conditions

$$\frac{l_1}{q_1} + y_1 = \frac{l}{q} + y, \; (l_1, q_1) = 1, l_1 \leqslant q_1 \leqslant \frac{2}{q|y|} \text{ and } q_1 > n^{\frac{3}{4}},$$

Putting $\rho_1 = e^{2i\pi \frac{l_1}{q_1}}$ and using lemma 5 we get $|T_1(j)| = \sum_{k \leqslant j^{\frac{1}{4}}} \rho_1^{k^4}$

$$< \frac{7 \cdot 83}{\epsilon_1^{\frac{1}{8}}} C^{\frac{3}{8}} n^{\frac{1}{8} + \frac{9\epsilon}{32}} (q \mid y \mid)^{-\frac{1+\epsilon_1}{8}}.$$

But $f(x) = \left(1 - \frac{x}{\rho_1}\right) \sum_{j=0}^{n-1} T_1(j) \left(\frac{x}{\rho_1}\right)^j + T_1(n) \left(\frac{x}{\rho_1}\right)^n$

and the result follows.

Lemma 18.

$$\sum_{M_2} \int_{M_2} |f^{15}(x)|^2 \, |dx| < \frac{10^{27 \cdot 8}}{\epsilon_1^{\frac{15}{4}}} C^{\frac{45}{4}} n^{\frac{97 + 135\epsilon + 45\epsilon_1}{16}}$$

Proof.

$$\int_{M_2} |f^{15}(x)|^2 \, |dx|$$

$$< 10^{27 \cdot 63} \frac{C^{\frac{45}{4}}}{\epsilon_1^{\frac{15}{4}}} n^{\frac{941}{160} + \frac{135\epsilon}{16} + \frac{93\epsilon_1}{32}} q^{-\frac{51}{40} - \frac{3\epsilon_1}{8}}.$$

Multiply this by q and integrate with respect to q from 1 to $n^{\frac{1}{4}}$.

9. *Lemma for the Whole Circle*

Lemma 19.

$$\int_R |f^{15}(x) - \sum_{q \leqslant n^{\frac{3}{16}}} \psi_\rho^{15}(x)|^2 \, |dx|$$

$$< 10^{60 \cdot 9} \frac{C^{\frac{45}{4}}}{\epsilon_1^{\frac{15}{4}}} n^{\frac{99 + 133\epsilon + 39\epsilon_1}{16}}.$$

Proof. As in Gelbeke Satz 17, we split the above integral into integrals over m-arcs, M_1-arcs, and M_2-arcs. The M_1-arcs are further subdivided into M_1' and M_1'' arcs, the first corresponding to $q_2 \leqslant n^{\frac{3}{16}}$ and the latter denote the remaining M_1 arcs.

Therefore

$$\int_R |f^{15}(x) - \sum_{q \leqslant n^{\frac{3}{16}}} \psi_\rho^{15}(x)|^2 \, |dx|$$

$$\leqslant 2 \sum_m \int_m |f^{15}(x)|^2 \, |dx| + 2 \sum_{M_2} \int_{M_2} |f^{15}(x)|^2 \, |dx|$$

$$+ 2 \sum_{M_1} \int_{M_1} |f^{15}(x) - \psi_\rho^{15}(x)|^2 \, |dx|$$

$$+ 4\, n^{\frac{3}{8}} \sum_{M_1'} \int_{R - M_1'} |\psi_\rho^{15}(x)|^2 \, |dx|$$

$$+ 4 \sum_{M_1''} \int_{M_1''} |\psi_\rho^{15}(x)|^2 \, |dx|$$

By lemmas 14, 18, 16 the first, second and third expressions together are less than

$$10^{60 \cdot 8} \frac{C^{\frac{45}{4}}}{\epsilon_1^{\frac{15}{4}}} n^{\frac{99 + 133\epsilon + 39\epsilon_1}{16}}.$$

By lemma 11 the fifth expression $< 10^{41 \cdot 1}\, n^{\frac{169}{39}}$ and by the inequality of lemma 12, the fourth expression $< 10^{43 \cdot 0}\, n^{\frac{1753}{330}}$

Hence the result follows.

10. The Main Lemmas

Lemma 20. If $\sigma(j) = r(j) - \eta \dfrac{\Gamma(\frac{15}{4} + j)}{j!} S(j, n^{\frac{3}{16}})$

where $$\eta = \frac{[\Gamma(\frac{5}{4})]^{15}}{\Gamma(\frac{15}{4})}$$

$$\sum_{j \leqslant n} |\sigma(j)|^2 < \frac{10^{60 \cdot 2}}{\epsilon_1^{\frac{15}{4}}} C^{\frac{45}{4}} n^{\frac{99 + 133\epsilon + 39\epsilon_1}{16}}.$$

Proof. The first $(n + 1)$ terms of

$$\Psi^{15}(x) = \eta \left(\frac{S_\rho}{q}\right)^{15} \sum_{j=0}^{\infty} \frac{\Gamma(\frac{15}{4} + j)}{j!} \left(\frac{x}{\rho}\right)^j$$

are the same as those of $\psi_\rho^{15}(x)$. Hence

$$\sum_{q=1}^{n^{\frac{3}{16}}} \psi_\rho^{15}(x) = \eta \sum_{j=0}^{n} \frac{\Gamma(\frac{15}{4} + j)}{j!} S(j, n^{\frac{3}{16}})\, x^j$$

$+ 14n$ terms with higher powers of x

and $f^{15}(x) - \sum_{q=1}^{n^{\frac{3}{16}}} \psi_\rho^{15}(x) = \sigma(0) + \sum_{j=1}^{n} \sigma(j)\, x^j +$ terms with higher powers of x.

By lemma 2 and lemma 19

$$\sum_{j \leqslant n} |\sigma(j)|^2 < \int_{-\frac{1}{2}}^{\frac{1}{2}} |f^{15}(e^{2i\pi y}) - \sum_{q \leqslant n^{\frac{3}{16}}} \psi_\rho{}^{15}(e^{2i\pi y})|^2 \, dy$$

$$< \frac{10^{60 \cdot 2}}{\epsilon_1^{\frac{15}{4}}} C^{-\frac{45}{4}} n^{\frac{99 + 133\epsilon + 39\epsilon_1}{16}}$$

Lemma 21. If B (ξ) is the number of positive integers $m \leqslant \xi$ for which the equation

$$m = \sum_{v=1}^{15} h_v^4, \qquad h_v \geqslant 0 \tag{1}$$

is not soluble, then

$$B(\xi) < 10^{192 \cdot 9} \frac{C^{\frac{45}{4}}}{\epsilon_1^{\frac{15}{4}}} \xi^{\frac{11 + 133\epsilon + 39\epsilon_1}{16}}$$

Proof. Let A (ξ) denote the number of positive integers $\leqslant \xi$ but $\not\equiv 0$ mod 16 for which (1) is not soluble. By lemma 20 for $\xi \geqslant n_0 + 1$

$$\sum_{\frac{\xi}{2} < m \leqslant \xi} \sigma^2(m) \leqslant \sum_{n=1}^{[\xi]} \sigma^2(m) < \frac{10^{60 \cdot 2}}{\epsilon_1^{\frac{15}{4}}} C^{\frac{45}{4}} \xi^{\frac{99 + 133\epsilon + 39\epsilon_1}{16}}$$

In A (ξ) − A $\left(\frac{\xi}{2}\right)$ terms of the sum $\sum_{\frac{\xi}{2} < m < \xi} \sigma^2(m)$ for which (1) is not soluble, $r(m) = 0$

and $\sigma^2(m) = \left(\eta \frac{\Gamma(\frac{15}{4} + m)}{m!} S(m, n^{\frac{3}{16}})\right)^2$

By lemma 8 $\frac{\Gamma(\frac{15}{4} + m)}{m!} > \frac{1}{2} m^{\frac{11}{4}}$

By lemma 7, if $16 \times n$ and m

$$S(n, \infty) > \frac{1}{10^{63 \cdot 57}}$$

and

$$S(m, n^{\frac{3}{16}}) > \frac{1}{10^{63 \cdot 57}} - \sum_{q > n^{\frac{3}{16}}} |A_q|$$

$$> \frac{1}{10^{63 \cdot 57}} - \sum_{q > n_0^{\frac{3}{16}}} |A_q|$$

But by lemma 6

$$\sum_{q > n_0^{\frac{3}{16}}} |A_q| < \sum_{q > n_0^{\frac{3}{16}}} 10^{19\cdot 83}\, q^{-\frac{11}{4}} < 10^{19\cdot 6}\, n_0^{-\frac{23}{64}}$$

and therefore $S\left(m, n^{\frac{3}{16}}\right) > \dfrac{1}{10^{6\cdot 58}}$

and $$\sigma^2(m) > \frac{\xi^{\frac{11}{2}}}{10^{132}}$$

Hence $$\left[A(\xi) - A\left(\frac{\xi}{2}\right)\right] \frac{\xi^{\frac{11}{2}}}{10^{132}} < \frac{10^{60\cdot 2}}{\epsilon_1^{\frac{15}{4}}}\, C^{\frac{45}{4}}\, \xi^{\frac{99 + 133\epsilon + 39\epsilon_1}{16}}$$

or $$A(\xi) - A\left(\frac{\xi}{2}\right) < \frac{10^{192\cdot 2}}{\epsilon_1^{\frac{15}{4}}}\, C^{\frac{45}{4}}\, \xi^{\frac{11}{16} + \frac{133\epsilon + 39\epsilon_1}{16}}$$

Now $$A(\xi) = \sum_{\nu=0}^{N} \left[A\left(\frac{\xi}{2^\nu}\right) - A\left(\frac{\xi}{2^{\nu+1}}\right)\right] + A\left(\frac{\xi}{2^{N+1}}\right)$$

where $$\frac{\xi}{2^N} > n_0 > \frac{\xi}{2^{N+1}}$$

$$< \left[A(\xi) - A\left(\frac{\xi}{2}\right)\right] \sum_{r=0}^{N} 2^{-\frac{\nu}{2}} + n_0$$

$$< \frac{10^{192\cdot 8}}{\epsilon_1^{\frac{15}{4}}}\, C^{\frac{45}{4}}\, \xi^{\frac{11}{16} + \frac{133\epsilon + 39\epsilon_1}{16}}$$

provided $\epsilon < \frac{1}{832}$.

By following the argument in the proof of Landau Satz 347, we get the inequality for B (ξ).

Lemma 22. If $N_4(n)$ denotes the number of integers m $(1 \leqslant m \leqslant n)$ for which

$$m = \sum_{\nu=1}^{4} h_\nu^4, \qquad h_\nu \geqslant 0$$

is soluble, then

$$N_4(n) > \frac{1}{10^{2\cdot 821}\, C}\, n^{\frac{23}{32} - \frac{9\epsilon}{16}}.$$

Proof. The number of solutions of the inequality $1 \leqslant h_1^4 + h_2^4 \leqslant n$, $h_1, h_2 \geqslant 0$ is greater than $\dfrac{n^{\frac{1}{4}}}{2\sqrt{2}}$.

For every integer m $(1 \leqslant m \leqslant n)$ the number of solutions of $m = h_1^4 + h_2^4$.

$$\leqslant 4\,\mathrm{C}m^{\epsilon} < 4\,\mathrm{C}\,n^{\epsilon}$$

Therefore $\quad \mathrm{N}_2(n) > \dfrac{1}{8\mathrm{C}\sqrt{2}}\, n^{\frac{1}{2}-\epsilon}$.

Consider all numbers $h^4 + z$, $h > 0$, z an integer, $\dfrac{n}{2} < h^4 < (h+1)^4 < n$

$$0 < z \leqslant n^{\frac{3}{4}}$$

and z of the form $h_1^4 + h_2^4$.

Corresponding to one value of h there are at least $\dfrac{1}{8\sqrt{2}\mathrm{C}}\, n^{\frac{3}{4}(\frac{1}{3}-\epsilon)}$ values of z for which no two numbers of the type $h^4 + z$ are the same.

The number of such h's $> \dfrac{2^{\frac{1}{4}}-1}{2^{\frac{1}{2}}}\, n^{\frac{1}{4}}$.

Hence $\quad \mathrm{N}_3(n) > \dfrac{2^{\frac{1}{4}}-1}{\sqrt{2}}\, n^{\frac{1}{4}}\, \dfrac{1}{8\sqrt{2}\,\mathrm{C}}\, n^{\frac{3}{8}-\frac{3\epsilon}{4}}$

and $\quad \mathrm{N}_4(n) > \left(\dfrac{2^{\frac{1}{4}}-1}{\sqrt{2}}\right)^2 n^{\frac{1}{4}}\, \dfrac{1}{8\sqrt{2}\,\mathrm{C}}\, n^{\frac{15}{32}-\frac{9\epsilon}{16}}$

and the lemma follows.

11. The Final Argument

THEOREM I. Every number greater than $10^{10^{88.39}}$ can be represented as the sum of 19 biquadrates.

Proof. Let n be a number which cannot be expressed as the sum of 19 biquadrates. The $\mathrm{N}_4(n)$ numbers $n - m$, where $0 < m \leqslant n$ and m is representable as the sum of 4 biquadrates, cannot be expressed as the sum of 15 biquadrates. Hence by lemma 21

$$\mathrm{N}_4(n) > \frac{10^{192\cdot 9}}{\frac{1.5.}{4}\,\epsilon_1}\, \mathrm{C}^{\frac{45}{4}}\, n^{\frac{11}{16}+\frac{133\epsilon+39\epsilon_1}{16}}$$

But by lemma 22

$$\mathrm{N}_4(n) > \frac{1}{\mathrm{C}\ 10^{2\cdot 821}}\, n^{\frac{23}{32}-\frac{9\epsilon}{16}}$$

Therefore

$$\frac{10^{192\cdot 9}\,\mathrm{C}^{\frac{45}{4}}}{\frac{1.5.}{4}\,\epsilon_1}\, n^{\frac{11}{16}+\frac{133\epsilon+39\epsilon_1}{16}} > \frac{1}{\mathrm{C}.\ 10^{2\cdot 821}}\, n^{\frac{23}{32}-\frac{9\epsilon}{16}}$$

or $$n^{\frac{1}{32}-\frac{142\epsilon+39\epsilon_1}{16}} < 10^{195\cdot8}\, C_{\epsilon_1}^{\frac{49}{4}\,\frac{15}{4}}.$$

It may be noticed, that the value of n mainly depends upon ϵ, ϵ_1 does not make any appreciable difference.

By putting $\epsilon_1 = 10^{-10}$, $\epsilon = \frac{1}{285\cdot4}$ we get the result.

THEOREM II. Under the hypothesis,* that a number cannot be expressed as the sum of two biquadrates in more than two ways, we prove that every number greater than $10^{10^{68\cdot6}}$ can be expressed as the sum of 19 biquadrates.

Proof. Under the above assumption,

if R (m) is the number of solutions of $h_1^4 + h_2^4 = m$, then

$$\sum_{v=0}^{m} \mathrm{R}^2(v) \leqslant 8\sqrt{m}$$

and $$\mathrm{N}_4(n) > \frac{1}{10^{2\cdot52}}\, n^{\frac{33}{32}}.$$

By making the corresponding changes in the lemmas we get

$$n^{\frac{1}{32}-\frac{117\epsilon+39\epsilon_1}{16}} < 10^{195\cdot5}\, C_{\epsilon_1}^{\frac{45}{4}\,\frac{15}{4}}$$

where n is a number which cannot be expressed as the sum of 19 biquadrates.

Put $\epsilon_1 = 10^{-10}$ and $\epsilon = \frac{1}{235\cdot5}$, the result follows.

It is a pleasure to record my thanks to Dr. S. Chowla for suggesting this problem to me and for the interest he took in the preparation of this paper.

* Hardy and Wright, *An Introduction to the Theory of Numbers*, Oxford University Press (1938), p. 333.

SOME ASPECTS OF THE PHYSICS OF WATER-TABLE RISE AND SALT MOVEMENT IN THE SOIL UNDER IRRIGATED CONDITIONS

By E. McKenzie Taylor

(From the Irrigation Research Institute, Lahore)

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Introduction

From the study of irrigation projects in various parts of the world, the rise of water-table after the introduction of irrigation seems to be inevitable. Irrigation is confined to arid and semi-arid areas. One of the chief characteristics of the soil of such areas is the presence of sodium salts. Although these salts may not exist in a harmful concentration in the surface soil at the commencement of irrigation, the ultimate appearance of the salts at the soil surface in the form of an efflorescence generally occurs. The rise of water-table and the appearance of salts at the soil surface have, therefore, been assumed to be associated phenomena, the latter being caused by the former. Until recently this view has been held in the Punjab. The reason for this supposed association in the Punjab is that surveys of areas of high water-table have been in progress for a number of years and in these areas large patches of salt land occur. In 1938 the surveys were extended to areas in which the water-table was situated at depths up to 40 feet below the natural surface. It was found that, under conditions of a deep water-table, salt was appearing at the soil surface and land deterioration at a fairly rapid rate was in progress. From these observations, it appeared that the rise of water-table and the appearance of salt were not necessarily associated phenomena.

Observations of the movements of the water-table in the Punjab, as indicated by well measurements in June and October, have been made for a long period of years. A study of these records has shown that in certain areas the rate of rise of the water-table decreases as the water-table approaches the natural surface and that finally a steady level, as indicated by the June measurements, appears to be attained. The soil profile in the Punjab usually consists of a soil crust containing clay overlying a grey alluvial sand from which clay is absent. It has been suggested[1] that when the water-table rising through the sand reaches the bottom of the soil crust, a " capillary fringe ",

five feet in height in the first year, is formed in the soil crust and that evaporation from the soil surface then reduces the rate of rise and finally controls the water-table level. The water-table would thus be stabilised at a certain depth below the natural surface depending upon the physical conditions in the soil crust. The problems presented are of considerable interest to soil physicists and of great practical importance in connection with the future of agriculture in irrigated areas.

An examination of the well records for an area in which the water-table appears to have been stabilised has been made by Malhotra.[2] His conclusions may be summarised as follows :—

(1) The observations can be divided into two periods: In the later period the seasonal annual fall in water-table between October and June is so great as to almost neutralise the seasonal annual rise from June to October.

(2) The steadiness of the water-table in the later period is probably not mainly due to increased evaporation from the water-table as this feature is reproduced in a sample of sixteen wells chosen at random, many of which are still so deep as to be beyond the reach of evaporating agencies.

The examination of the records made by Malhotra having shown that the water-table has been stabilised at depths ranging from 18 feet to 3 feet, evaporation from the soil surface as the factor controlling the water-table rise appears to be discounted since evaporation is unlikely to be equally operative over such a wide range of water-table depths.

The capillary theory of water movement has formed the subject of many laboratory investigations. Two methods have been adopted in these studies; either the rise of water through columns of dry sand has been examined or else the " capillary pull " has been measured by applying suction to a saturated soil. Attention has been directed by Keen[3] to the small part played by capillarity in moisture movement in a soil. Keen[4] has stated as a result of his investigations that water having reached a depth of six feet in the average soil does not return to the surface by means of evaporation. If this is accepted, it follows that any water that has reached a depth of six feet in the soil must be regarded as a permanent addition to the soil moisture except in so far as it may be removed by the transpiration of vegetation.

In the light of recent work by Afzal and Vaidhianathan,[5] the depth of six feet stated by Keen may be an over-estimate. Keen used cylinders six feet in depth for his experiments and determined the losses of water by measuring the depth of the water-table as indicated in an iron pipe placed in

the cylinder. Afzal and Vaidhianathan have shown that such a method of measurement is incorrect since the level of the water in the pipe is affected by the pressure deficiency developed in the water films in contact with the soil particles. As the water-table depth measured by means of a pipe sunk in the soil is lower than the true depth, the results recorded by Keen exaggerate the effect of evaporation. The depth of soil in which the moisture content is affected by evaporation is likely to be less than six feet under the climatic conditions in England.

From the above discussion it follows that if evaporation is to be a controlling factor in water-table depth, the water-table must be situated at such a depth that it can influence the moisture content of the top six feet of soil. Keen[6] states that the capillary rise does not exceed three or four feet. The two statements of Keen regarding the depth affected by evaporation and the height of capillary rise taken together indicate that the water-table must be situated within ten feet of the soil surface if it is to be affected at all by evaporation. There appear to be, therefore, two distinct general cases for examination (*a*) when the water-table is situated within ten feet of the soil surface and (*b*) when the water-table is at a depth greater than ten feet from the soil surface.

In order to discuss the vertical distribution of water under experimental conditions and in the field, it is necessary to have standards to which reference can be made. As has already been pointed out two methods of experimentation, employing either dry or saturated materials, have been used. Neither of these initial states are common in the field and as a consequence certain important conditions in the field have been overlooked and the results of the investigations have only a limited application. Veihmeyer[7] has shown that when a soil is irrigated, the soil is raised to field capacity moisture content to a depth for which the water supplied is sufficient. Field capacity may be defined as the maximum moisture content to which a soil can be wetted under the action of gravity in the field. That irrigated soils might have a zone of permanent field capacity situated some distance below the surface does not seem to have been realised previously because deep borings have not been examined. As field capacity is a condition of the soil with a moisture content that can be defined it forms a convenient starting point for field studies. According to the classification given by Keen[8] the moisture stages lower than the capillary stage are the funicular stage and the pendular stage. The most active agent producing these stages under field conditions is evaporation. The moisture content at field capacity appears to be a well defined point in these stages. For the purpose of this paper the funicular end pendular stages below field capacity will be classified

together under the term 'pellicular stage'. The higher unsaturated moisture stage above the field capacity and the true capillary stage will be grouped together as the 'capillary stage'. When the pores are completely full of water and the water is free as a body to take part in movements due to gravity the moisture conditions will be termed 'the Water-table stage.'

Experimental

Under irrigation conditions, Veihmeyer[9] has shown that water applied to the soil surface moistens the soil to field capacity to a depth for which the water supplied is sufficient. If the water applied is enough to raise the moisture content of the whole of the pellicular zone to field capacity, then the soil throughout its depth to the water-table, except for a shallow capillary zone immediately above the water-table, will be at field capacity. Under these conditions, the moisture throughout the depth of soil to the water-table is in equilibrium with gravity as a corollary of the definition of field capacity. It appeared probable, therefore, that no upward movement of water from the water-table could take place through a soil at field capacity whatever the distance of the water-table below the surface.

When evaporation commences, the field capacity stage at the soil surface passes to the pellicular stage. As evaporation proceeds, the depth of the pellicular stage zone gradually increases until a certain maximum depth of development is reached. During the development of the pellicular stage zone the soil above the shallow capillary zone will still be at field capacity and, hence, it seemed probable that no water could be raised from the water-table to the pellicular stage zone to replace that lost by evaporation. If this view proved to be correct, it would follow that so long as a field capacity stage zone is situated between the developing pellicular stage zone and the capillary stage zone evaporation could have no effect upon the water-table.

In order to test the above views, a series of experiments was conducted. In the first experiment one glass tube was filled with dry sand and a second with sand saturated with water. The saturated sand column was allowed to drain, so that the column came to field capacity. The two columns of sand were then placed vertically in a trough of coloured water and the movement of water in the sand colums observed. It was found that a rapid rise occurred in the dry sand column but that there was no tendency for the coloured water to enter the sand column at field capacity. Evaporation was allowed to take place from the field capacity sand column but even after fifteen days no water had risen from the water-table into this tube though

there had been a small amount of diffusion of the dye into the base of sand column. From this it appears that during the development of the pellicular stage zone the water being evaporated at the sand surface is not replaced by water drawn from the water-table. The condition of the two columns after fifteen days is shown in Fig. 1.

In order to obtain further information on the effect of the field capacity zone on evaporation and the water-table, a series of sand columns of varying depths and at field capacity were set up in troughs of coloured water. It was noted that no water entered the sand columns at the commencement of the experiment. In order to rapidly establish pellicular stage zones, dry sand was added to the top of the field capacity zones and the time taken before coloured water entered the tubes was noted. It was observed that water rapidly passed from the top of the field capacity zone into the dry sand forming pellicular stage zones. The results are shown in Table I and Fig. 2.

TABLE I

Time taken before water passes into columns of sand at field capacity after the establishment of a surface pellicular stage zone

Original depth of field capacity zone	Time
6 inches	6 minutes
9 „	60 „
12 „	720 „
27 „	No rise in 15 days

The results of Table I clearly show that as the depth of the field capacity stage zone is increased the time taken for the effect of the establishment of the pellicular stage zone to be felt on the water-table also increases. It was noticed that the movement of the coloured water into the sand columns only occurred after the complete conversion of the field capacity zone into a pellicular stage zone. The conditions in this experiment are extreme since under field conditions it is impossible to have an air dry zone directly in contact with a field capacity stage zone.

These experiments lead to the important conclusion that so long as the field capacity stage zone exists between a pellicular stage zone and the water-table, evaporation at the surface of the soil can have no effect upon the water-table, and, therefore, the control of the water-table level cannot be established by evaporation. The experiment also has an important application to salt movement which will be dealt with later.

The Examination of the Moisture Distribution in Soil Profiles under Field Conditions

A large number of borings have been made in Punjab soils with the object of studying the distribution of water in the soil profile down to the water-table. The results of borings illustrating the various conditions encountered will now be given and discussed.

Case I A. The Water-table within six feet of the surface.—The moisture distribution of a profile complying with this condition is given in Table II.

TABLE II

Depth in feet	Moisture %	
1	15·2	Soil Crust
2	21·2	
3	19·2	
4	24·7	
5	26·1	Sand
6	29·1	

Soil Crust 5′ 0″ thick
Water-table 5′ 9″

In this case there is no well marked zone of field moisture capacity. The second and third feet are below and the fourth foot is above the field capacity. The higher moisture contents in the fourth and fifth feet are due to the capillary stage zone being at these depths. In this profile the field capacity zone has been eliminated and there appears to be a direct connection between the pellicular stage and the capillary stage zones. Evaporation at the surface will, therefore, withdraw water from the water-table exerting some control over its depth.

Case I B. The Water-table situated between sixth and tenth feet from the natural surface.—The moisture distribution in a profile of this type is given in Table III.

TABLE III

Depth in feet	Moisture %		
1	15·2	Soil Crust	Soil Crust 7′ thick Water-table 7′ 3″
2	16·5		
3	17·4		
4	20·8		
5	20·4		
6	20·8		
7	25·5		
	Sand		

The first three feet of this profile are occupied by the pellicular stage zone. The fourth, fifth and sixth feet are at field capacity. The seventh foot having a higher moisture content than field capacity is situated in the capillary stage zone. From the experimental work it will be seen that since a field capacity stage zone is situated between the water-table and the pellicular zone, evaporation from the surface will not affect the water-table until the field capacity zone is eliminated. Under normal conditions of evaporation, the extension of the pellicular stage zone below six feet will be a slow process.

Case 2. *The Water-table situated below a depth of ten feet.*—An example of the moisture distribution in this type of profile is given in Table IV.

In the above profile the pellicular stage zone has extended to the eighth foot. Between the eighth and twelfth feet the soil is at field capacity. The thirteenth and fourteenth feet are in the capillary zone and at the fifteenth foot the water-table was encountered. In none of the bores made in the Punjab has the pellicular stage zone, under irrigation conditions, been found to extend beyond the eighth foot, the more usual maximum depth being six feet.

TABLE IV

Depth in feet	Moisture %		
1	6·2	Soil Crust	Soil Crust 15′ thick Water-table 15′ deep
2	4·1		
3	5·5		
4	8·1		
5	9·1		
6	13·2		
7	15·2		
8	23·2		
9	26·4		
10	25·4		
11	24·0		
12	26·4		
13	29·3		
14	34·5		
15	39·8		
		Sand	

It may be concluded, therefore, that as there is a four-foot zone of field capacity below this depth, water cannot be raised from the water-table to the pellicular zone and, hence, evaporation from the soil surface will exert no influence on the water-table.

An example of the moisture distribution in a soil profile taken in land which has never been irrigated is given in Table V.

TABLE V

Depth in feet	Moisture %		
1	7·2		
2	10·4		
3	11·3		
4	11·8		
5	11·7		
6	12·2		
7	13·6		
8	10·9		
9	14·6		
10	16·5	Soil Crust	Water-table 22′ deep
11	19·0		
12	18·4		
13	20·2		
14	19·8		
15	20·0		
16	18·0		
17	20·9		
18	21·0		
19	22·1		
20	22·9		
21	24·8		
		Sand	

In this case the soil crust extended to a depth of twenty-one feet and the water-table was situated at a depth of twenty-two feet. The average annual rainfall in this area is about fourteen inches and occurs mainly during the monsoon period. In this case the pellicular stage zone occupies the first twelve feet. Between the thirteenth foot and the eighteenth foot a well-marked zone of field capacity exists, the capillary stage zone occurring between the nineteenth and twentieth feet. It appears from this profile that under extreme conditions of evaporation in the Punjab, a zone of field capacity still persists and that the water-table may be protected from loss of water by evaporation.

The moisture distributions in these soil profiles clearly exhibit similarities to those experimented upon in the laboratory and they are, therefore, capable of interpretation in the light of the laboratory experiments.

Some Applications of the Observations

(*a*) *The control of the rise of water-table by evaporation.*—It was pointed out early in this paper that a suggestion had been put forward that on the water-table reaching the bottom of the soil crust a capillary fringe of five feet was formed and that evaporation from this fringe conuterbalanced additions to the water-table thus stabilizing it.

A large number of borings in deep water-table areas have shown that the lower layers of the soil crust are at field capacity. As these deep water-tables are situated in coarse sand, it is impossible for them to have influenced the moisture content of the crust at their present levels. The soil borings in the high water-table areas have shown that a capillary stage zone does not exceed two feet in depth when the water-table reaches the bottom of the soil crust. Beyond a depth of water-table of ten feet, the capillary stage zone is overlaid by a field capacity zone. Experimental evidence has been produced to prove that no water can be raised from the water-table to the pellicular stage zone through a field capacity zone. The explanation of the stabilizing of the water-table below a depth of ten feet based on evaporation is, therefore, untenable.

If the soil crust is less than ten feet in thickness, the rising water-table will touch a soil crust at field moisture capacity in the lower layers under irrigation conditions. During the development of the pellicular stage zone, so long as the soil above the capillary stage zone remains at field capacity, no water lost from the surface can be replaced by water derived from the water-table. If the pellicular stage zone is allowed to develop to its maximum then the field capacity zone may be eliminated and direct contact established between the pellicular stage zone and the capillary stage zone.

Under these conditions water derived from the water-table would replace, to some extent, that lost by evaporation at the soil surface. Under irrigation conditions, the greatest depth to which the pellicular stage zone has been found to extend is about six feet. The observed maximum height of the capillary stage zone is about two feet. It can be concluded, therefore, that if the depth of the water-table is less than ten feet evaporation from the soil surface may effect the water-table level under extreme conditions. It seems more probable, however, that the water-table will have to be much nearer the surface than ten feet for control to be established by evaporation.

(*b*) *The rise of water-table resulting from applications of irrigation water.*—The rise of water-table, as indicated by well observations, appears to take place in two stages, the first stage being an apparent rise and the second stage a true rise. During the summer of 1939, observations were made on a series of wells to determine the effect of rainfall on their behaviour. The record of one such well is given in Fig. 3.

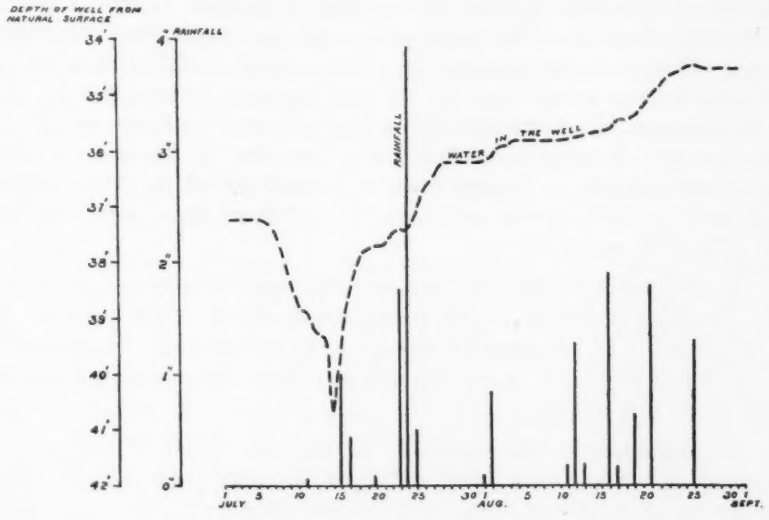

FIG. 3

Behaviour of a well with reference to Rainfall

From Fig. 3 it will be seen that the water-table reached its maximum depth, according to the well level, about the 14th of July. A rainfall on the 15th of July caused a sudden rise in the well level. This rise was approximately three feet with a rainfall amounting to 1½ inches. It will be seen that

the quantity of water falling as rain could not possibly account for the addition of this amount of water to the water-table. Between the 22nd and 25th of July further heavy rainfall occurred. On this occasion the sudden rise in well level is much less marked. A further rainfall occurred on the 1st and 2nd of August. While the same sudden rise is still present its magnitude is much less than that which had taken place previously. Rainfall after the 10th of August produces a gradual rise to the maximum water-level in the well and in this period no evidence of a sudden rise is present.

The apparent rise in the well level on the 15th and 16th of July appears to be due to the reduction in the pressure deficiency in the films in the pellicular stage region and does not represent a true addition of water to the water-table. After the pressure deficiency has been reduced still further by subsequent rains, as indicated by the gradually decreasing sudden rise, then the further rise that takes place in the water-table with subsequent rainfall may be regarded as a true addition of water to the water-table. The same phenomenon can be observed when irrigation water is applied to the soil surface. If observation pipes are installed in an area to be irrigated an immediate rise of the water in the pipes takes place soon after the irrigation has commenced. This apparent rise of water-table is much greater than can be accounted for by the quantity of water applied. The initial rise is due to the elimination of the pressure deficiency in the pellicular stage region and does not represent an addition to water-table. If the quantity of irrigation water applied is large enough to convert the whole of the pellicular stage zone to field capacity and a surplus still exists, then true additions to the water-table occur.

In the Punjab considerable use has been made of well records to determine the effect of rainfall on the water-table level and of the probable effect of lining canals on additions by seepage to the water-table. It appears that these subjects now need to be reinvestigated in the light of the phenomenon discussed in this section.

(*c*) *The effect of the water-table on the rise of salts resulting in salt efflorescence.*—It has been stated earlier in this paper that the rise of salts and the rise of water-table were until recently regarded as associated phenomena. Recent work, which has been quoted, has shown that the rise in salts in the soil is occurring in both high and low water-table areas and therefore, there appears to be no essential connection between the two conditions. The reason for this now becomes evident.

The soil crust in the Punjab in the area west of longitude 74° E. usually contains sodium salts, mainly sodium sulphate. When land is brought

under irrigation the salts in the surface layers of the soil are removed to a lower depth, and a zone of salt accumulation is formed. If this zone of salt accumulation is formed within six feet of the surface then it is situated within the zone in which the pellicular stage is likely to develop and may as a result of evaporation move upwards. The rate of this movement upwards will depend upon the quantity of irrigation water supplied. If the quantity of water is large as in the case of crops such as sugarcane and berseem then the pellicular stage gets little chance of developing to the maximum extent and, hence, the upward movement of salt must be slow. If on the other hand light irrigations are given, as in the case of wheat, then a greater development of the pellicular stage zone results and the movement of the salt upward becomes more rapid. Observations show that deterioration due to the rise of salts is more rapid in the winter under the wheat crop than it is in the summer when the more heavily irrigated crops are grown.

If on the introduction of irrigation the zone of accumulation of salt is formed below a depth of six feet, then it is situated in a zone which is mainly in the field capacity stage from which water does not return to the surface. The upward movement of salt cannot, therefore, take place when the zone of accumulation of salts is below a depth of six feet. Further, as the bottom of the zone of field capacity is in contact with the capillary stage zone and as it has been shown that under these conditions water from the water-table cannot pass upward, it must be concluded that the water-table can have no influence on the upward movement of salts when it is situated at a depth below ten feet from the surface.

These conclusions have an important application to the development of irrigation projects. Irrigation is only used under arid and semi-arid conditions. It is now generally recognised that the soils of such regions are characterised by the presence of sodium salts in the soil profile. If deterioration of land due to the upward movement of salts is to be avoided then it is essential that in the development stages of an irrigation project the amount of water applied should be sufficient to ensure that the sodium salts are washed below a minimum of depth of six feet from the surface. In order to secure this result rice should be the initial crop in any irrigation project. To determine whether the results desired have been achieved, analyses of soil profiles are essential.

While it has been recommended above that the minimum depth to which salt should be washed should be six feet, a greater depth than this is essential if maximum crop production is to be secured. Plant roots go much deeper than was formerly supposed. If salt is present in the normal

root zone of a crop, then the yields are likely to be low. It is suggested, as a result of reclamation work, that the aim should be to wash the salts below a depth of ten feet from the soil surface.

(*d*) *The effect of moisture movements on land reclamation.*—The reclamation of land from sodium salts consists essentially in removing the salts to a depth from which they cannot return to the surface or harm the crop and in breaking down the residual sodium clay in the upper layers of the soil by the growth of rice.

Reference has already been made to the work of Veihmeyer in which he showed that it was possible to moisten the soil to field capacity to a depth for which the water supplied was sufficient. Keen[10] states " As the surplus (water) percolates downward through the macro-pore-space toll is levied on it by each crumb in turn ", and, again, " The soil becomes wet up to what is called field capacity, and it is only the surplus water that percolates further to the water-table ". These statements appear to give a picture which does not fit in with field observations.

It can be demonstrated readily in the laboratory that if a soil column is brought to field capacity moisture content, then any surplus water placed on the surface of the soil *displaces* downwards water already present in the soil and that the surplus water does not itself percolate and pass to the water-table. This displacement downwards of water present in the soil at field capacity is of considerable importance in land reclamation. If the water surplus to field capacity merely percolated downwards then the removal of the salts, already in solution in the water in the soil at field capacity, would be impossible. Since the movement of the water in a soil at field capacity is one of displacement and not percolation, reclamation is a relatively rapid process.

(*e*) *The conditions for permanancy of land reclamation.*—A question often asked in connection with land reclamation is " Is land once reclaimed, permanently reclaimed ?" It is now possible to answer this question. Since it has been demonstrated that water in the permanent field capacity stage zone is not moved by evaporation at the surface it follows that if salt is washed into such a permanent zone then it will be impossible for it to return to the pellicular stage zone in which upward movement resulting from evaporation can take place. As the maximum depth observed in the Punjab for the pellicular stage zone, under irrigation conditions, is six feet it follows that reclamation is permanent if the salt is washed below this depth from the natural surface. If the water-table is situated within six feet of the surface then if the pellicular stage zone fully develops, it is possible that salt may

commence to return to the soil surface. Observations after reclamation show this to be an extremely slow process. In one area reclaimed in 1931 the water-table is situated at a depth of three feet below the natural surface. The analysis of the soil profile shows that there is no tendency for the salt to return and this is confirmed by crop yields in the area. Even if there were a tendency to return, all that is necessary to control the full development of the pellicular stage zone is the growing of crops, such as sugarcane and berseem, requiring heavy irrigation to maintain field capacity conditions.

It has also been suggested that salt removed from one area during reclamation and added to the water-table may lead to the appearance of salt in another area not previously affected. From the discussion of the conditions under which evaporation can affect a water-table it now becomes clear that if salt is washed into the water-table and that water-table is at a greater depth than ten feet in any area then reclamation cannot affect the adjoining areas since no water can rise from a water-table through a zone at field capacity.

Summary

1. The importance of the presence of a zone of field capacity moisture content on the movement of moisture in a soil has been investigated in the laboratory.

2. Observations have been recorded which show that under irrigated soil conditions in the Punjab there is a permanent field capacity moisture zone situated below a depth of six feet from the natural surface.

3. The presence of the field capacity zone has been shown to prevent water rising from a water-table as a result of evaporation at the soil surface. It follows that evaporation cannot be a factor controlling water-table level when the water-table is at a greater depth than ten feet. If the water-table is situated within ten feet of the surface then some control may be established by evaporation if the pellicular stage zone is completely developed. This condition rarely occurs under irrigation.

4. It has been shown that there is no essential connection between the rise of water-table and the rise of salts in the soil. The application of the movement of moisture in a soil to the processes of land deterioration, reclamation and its permanency have been discussed.

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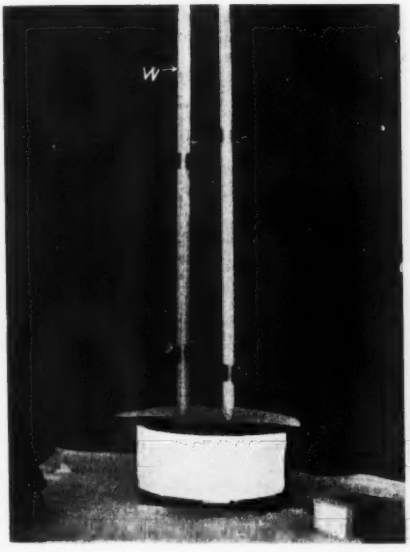

FIG. 1

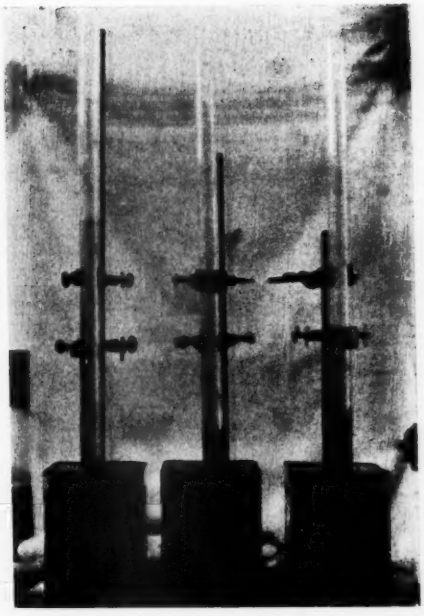

FIG. 2

Photograph taken after 26 hours

CLASSICAL THEORY OF SPINNING PARTICLES: ERRATA

By H. J. Bhabha, Ph.D.

(*Vol. XI, No. 4, April 1940, Section A, pp. 247-267*)

The following misprints have occurred :—

The third equation of (3) is $S_\mu''' = \ddot{\dot{S}}_{\mu\nu} v^\nu$.

The third term of (33) is $g_2\, v^\mu\, \dot{S}_{\mu\sigma}\, \overset{\text{in}}{F}{}^{\sigma\nu}\, v_\nu$. There should be no dot over F.

In the second line from the bottom on p. 254 *read* (29) instead of (28).

The last term of (47) is $\overset{\text{in}}{F}_{\mu\nu}\, v^\nu\, v_\sigma$ not $\overset{\text{in}}{F}_{\mu\nu}\, v^\nu\, v_\mu$.

In line 19, p. 258 *read* $\ddot{\dot{S}}_{\mu\nu}$ instead of $\ddot{\dot{S}}_{\mu\nu}$.

The last term of (49) should be $d\ (S'\, \ddot{S}\, \dot{v})$ not $d\ (S'\, \dot{S}\, \dot{v})$.

In the third line of the new section on p. 259 *read* $M\dot{v}_\mu$ instead of Mv_μ.

The sentence after (52) should end " of magnitude H_0. "

The thirteenth term of (65) is $c_{13}\, S_{\mu\nu}\, \ddot{S}^{\nu\rho}\, \dot{v}_\rho$.

The fifth term of the table on p. 264 should be $v_\lambda\, \dot{S}_{\mu\nu}\, S''^\nu$ instead of $\dot{v}_\lambda\, \dot{S}_{\mu\nu}\, S''^\nu$.

In the third line on p. 265 *read* " third " instead of " last ".

In the expression for $\overset{\text{self}}{T}_\mu$ on p. 266 the second term in the second line from the bottom should be $(d + \frac{2}{15})\, S_{\mu\nu}\, \dot{S}^{\nu\rho}\, \dddot{v}_\rho$ instead of $(d + \frac{2}{15})\, S_{\mu\nu}\, \dot{S}^{\nu\rho}\, \ddot{v}_\rho$.

ON ELEMENTARY HEAVY PARTICLES WITH ANY INTEGRAL CHARGE: ERRATA

By H. J. Bhabha, Ph.D.

(*Vol. XI, No. 4, April 1940, Section A, pp. 347-368*)

The following misprints have occurred :—

The expression at the bottom of p. 354 should contain c^2 after ΔM.

In the formula for $1/\tau$ on p. 355, line 8 *read* g^2 instead of δ^2.

In line 14, p. 356, *delete* " so that $(\mathbf{p}_f, \mathbf{p}_0) = \cos\theta$."

The equation at the top of p. 358 should not be numbered (13).

In equation (17) *read* dQ instead of $d\theta$, and g'_2 instead of g'_1.

In line 2, p. 360 *read* $(M/\mu)^2$ instead of $(M/m)^2$.

In line 1, p. 361 *read* (30) instead of (29).

The last word of the subtitle on p. 362 should be " Photons " *not* " Protons ".

In the sentence immediately after (36) on p. 362 *read* " process " instead of " processes ", and "(35) or (36) " instead of " (35) and (36) ".

In the last line before (37) *insert* " θ " between " direction " and "is".

In the first term in square brackets of (40) *read* c^2p^2 instead of p^2 in the numerator and $(\Delta Mc)^2$ instead of $(\Delta M)^2$ in the denominator.

In (44) *read* e^4 instead of c^4.

Equation (46) should read

$$al = \int_{\epsilon_0}^{\epsilon} \frac{d\,\epsilon'}{\log \epsilon'} = \overline{\mathrm{Ei}}\,(\log_e \epsilon) - \overline{\mathrm{Ei}}\,(\log_e \epsilon_0).$$

In line 5, p. 366 *read* " quarter " instead of " half ".

In line 16, of the *Summary* on p. 367 *read* 10^{-25} cm.^{2} instead of 10^{-27} cm.^{2}

In line 3, p. 368 *read* " track " instead of " tract ".